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AFRPL-TR-67-61

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**(UNCLASSIFIED TITLE)**

**CHARACTERIZATION  
AND  
EVALUATION  
OF LIGHT METAL HYDRIDES**

LOCKHEED PROPULSION COMPANY  
REDLANDS, CALIFORNIA

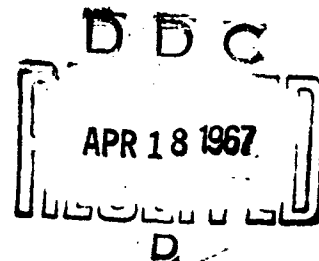
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LPC Report No. 716-Q-5

(UNCLASSIFIED TITLE)

CHARACTERIZATION AND EVALUATION OF LIGHT METAL HYDRIDES

Lockheed Propulsion Company  
P. O. Box 111  
Redlands, California

February 1967

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## FOREWORD

(U) This is the fifth quarterly report issued under Contract No. AF 04(611)-11219. This report was prepared by W. E. Baumgartner, W. S. Baker, G. E. Myers, and Y. A. Tajima, Chemistry Department, Lockheed Propulsion Company (LPC). Contributors to the work reported herein include W. D. Allan, G. R. Cann, K. W. Cox, D. G. Riordan, D. R. Szymanski, and W. Wooten.

(U) The program is monitored by the Air Force Rocket Propulsion Laboratory (AFRPL), Edwards, California (Lt. W. E. Anders).

(U) This report contains information regarding the use and the performance of light metal hydrides in solid propellants and is classified CONFIDENTIAL

(U) Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange of and stimulation of ideas.

William Ebelke  
Colonel, USAF  
Chief, Propellant Division



## UNCLASSIFIED ABSTRACT

Evaluation of a light metal hydride in CMDB propellants was continued. Distinct improvements in processability were observed with recent batch production lots. By contrast, the laboratory scale continuous process to-date has produced a material that is more difficult to process but expected to afford higher combustion efficiency.

Evaluation of these materials in combination with P-BEP/TVOPA binders was hampered by difficulties in achieving reproducible cure. These difficulties were overcome by pretreatment of the prepolymer, and by changing the mode of cure catalyst addition.

A theoretical-experimental program upon the shelflife of LMH propellant was completed. Reasonable agreement between observed and predicted failure times was obtained and estimates of motor shelflife were made.

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SECTION I  
INTRODUCTION

(C) 1. TASK I - CHARACTERIZATION AND EVALUATION OF  
BERYLLIUM HYDRIDE

The objective of this task is to characterize and evaluate various grades of beryllium hydride for application in solid propellant systems, particularly in composite modified double-base (CMDB) propellants. Other systems of interest, e. g.,  $\text{NF}_2$  binder propellants, are also utilized in the evaluation.

This report contains data on recent production lots of Beany indicating continued improvements in the manufacturing process. Especially noteworthy is the successful incorporation of continuous-process material in a high theoretical impulse formulation.

Difficulties in curing a PBEP binder were investigated by infrared spectroscopy, and an  $\text{NF}_2$  binder system is ready for motor tests.

(C) 2. TASK II - LIGHT METAL HYDRIDE PROPELLANT SHELF LIFE

This part of the report constitutes a summary report of the work performed under this contract (Task II) in arriving at the ability to predict light metal hydride propellant shelf life. This report reviews the approach taken in analyzing the problem, and it summarizes the experimental data and the conclusions reached. It should be noted that it was not the purpose of this task to provide an evaluation of optimized  $\text{AlH}_3$  material. The objective was to conduct a physico-chemical investigation of the factors affecting the shelf life of propellants containing gas-generating ingredients in order to establish a theoretical basis for predicting shelf life.

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## SECTION II

TASK I - CHARACTERIZATION AND EVALUATION  
OF BERYLLIUM HYDRIDE

## (C) 1. SUMMARY

The objective of this task is to characterize and evaluate various grades of Beany<sup>1</sup> for application in solid propellant systems, emphasizing application in composite modified double-base (CMDB) propellants. To permit a meaningful evaluation of the various materials (e. g., materials produced by different synthesis routes; lot-to-lot variations; different crystal structures), an effort was made during the early part of the program to define the evaluation criteria; specifically, a program of small-motor firings (1½ to 3-pound motors) was conducted (Ref. 1) to establish a range of Beany CMDB propellant formulations affording high specific impulse efficiency at high Beany loading (15 percent).

During the report period, efforts were continued to apply these criteria to the evaluation of current pilot plant Beany materials produced by the Ethyl Corporation and to compare the pyrolytic material with the higher density, crystalline form. In addition, efforts were made to expand the range of applicable propellant systems to include higher performance CMDB propellants and NF propellants. Specifically, the following laboratory tasks were completed during this report period:

Twelve samples of new Beany lots were evaluated in a 17 percent LMH-2 formulation. Three of these lots, both as-received and after processing, were the best so far produced with respect to processibility. After being ground, all lots were successfully passivated by heating in air for 24 to 72 hours at 110°C.

Samples from the bench scale continuous reactor were incorporated in a 17.5 percent LMH-2/TNEOC formulation by grinding and using a high shear mixer. A firing test of this material is highly desirable because of potential cost savings and possible efficiency gains associated with a smaller average particle size.

Firing tests of dense LMH-2 (Ethylene) grains indicated that the combustion efficiency of Ethylene is equivalent to or slightly better than that of Beany control motors.

Difficulties with the cure of a new lot of PBEP were investigated by infrared spectrometry. Cures were obtained by treating the PBEP to remove acidic constituents and by using FEAA-coated AP.

<sup>1</sup> The term "Beany" is used throughout this report to designate amorphous pyrolytic BeH<sub>2</sub> (density 0.65 g/cc), while "Ethylene" is used to designate the crystalline material form.

Specific surface of lot 79 was measured by Krypton adsorption. Values of 1.3 and 2.0 meters<sup>2</sup>/gm were obtained, respectively, for the as-received and the ground material.

(C) 2. TECHNICAL EFFORT

a. Evaluation of Amorphous Beryllium Hydride (Beany)

Twelve new lots of Beany production from Ethyl Corporation were evaluated in the LPC 1032C formulation (17 percent Beany, 47.1 percent NIBTN, Table I).

Photomicrographs of five lots (Figure 1) show typical lot-to-lot variations in particle size and structure. The evaluation procedure consisted of mixing each lot in the "as-received" condition to establish relative viscosity and reactivity. Viscosities were off scale for nine lots (Table II), but lots B474, B475, and B478 were within the processible range (on-scale readings). These three lots were the most processible of all the lots received to date. Five lots gave low propellant densities indicating that passivation would be necessary even if the materials were to be used without grinding. From the photomicrographs, a striking difference is evident between the first lot of the series (B464) and succeeding batches. Average particle size for lot B464 (<80 microns) is more than double that of the other lots, and the sub-particle size, more clearly evident under a stereomicroscope, is significantly smaller. Characteristic of this type of particle is the diffuse, popcorn-like core, suspected to be porous ("wicking" or "sponge" effect when the material is mixed with propellant plasticizers). The cause of this structure in lot B464 is believed to be residual traces of lithium in the reactors which had been used in a preceding run to make lithium-doped feed stock for the production of crystalline hydride (Ethylene).

Confirming previous results for materials of similar particle structure, lot B464 could not be mixed and cast in the 17 percent hydride test formulation. The remaining lots were successfully mixed in the as-received condition and flowed under vibration although mix viscosities were high and off-scale on the Brookfield viscometer (T-bar E, 20 rpm) for all except the three lots noted above (Table II).

Grinding was conducted under arbitrarily selected conditions (10-20 gm charge, size 000 ball mill jar, forty 1/2-inch borundum stones) for 30 minutes. Remixes made with the ground materials showed the usual improvement in mix viscosities; cured propellant samples were more porous than those made with the as-received hydrides because of the increased reactivity produced by grinding.

After grinding, lots B471 and B472-3 were the most reactive as evidenced by their low propellant densities. These lots were apparently high in chloride content (Table III) and had the lowest bulk densities of those measured. A general correlation between bulk densities and processibility was observed previously; this correlation is apparent in the present series. The two highest bulk density lots, B474 and B475, were superior (lowest mix viscosities) throughout the evaluation tests.

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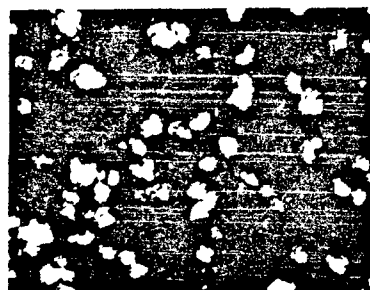
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TABLE I  
PROPELLANT FORMULATIONS

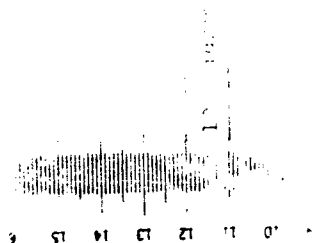
<u>Propellant</u>	<u>1032B</u>	<u>1032C</u>	<u>035-8</u>	<u>035-10</u>	<u>035-10A</u>
PNC	10.85	10.00	---	10.20	11.07
DEGDN	3.90	3.90	---	3.98	4.03
NIBTN	50.10	47.10	---	48.06	54.27
2-NDPA	---	1.00	---	1.02	1.07
Resorcinol	---	1.00	---	1.02	---
TNEOC	---	---	---	---	12.09
PBEP	---	---	8.80	---	---
TVOPA	---	---	26.40	---	---
TPMTI	---	---	0.70	---	---
FEAA	---	---	0.03	---	---
LMH-2	15.00	17.00	14.00	15.31	17.47
AP	20.15	20.00	---	20.41	---
<u>Theoretical</u>					
$I_{sp}^{1000}$ , 14.7 (lbf-sec/lbm)	303.3	305.3	---	---	---
$T^*$ ( $^{\circ}$ K)	2570	2346	---	---	---
$T_s^*$ ( $^{\circ}$ K)	2202	1928	---	---	---
Density (g/cc)	---	1.307	---	1.333	1.280
VSL (%)	---	60.53	---	53.67	43.01

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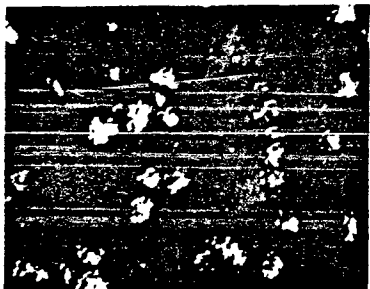
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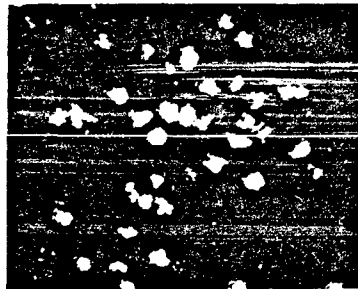
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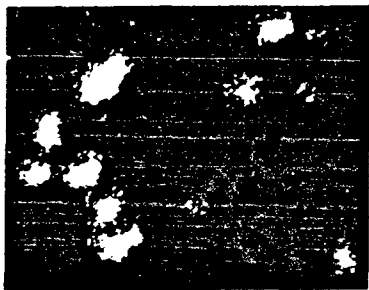
scale



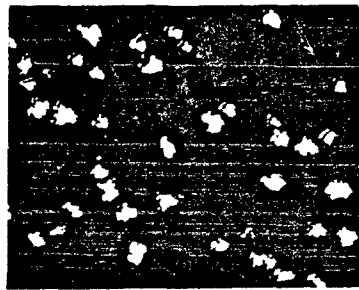
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479



Lot 464



469

Figure 1 Amorphous Beryllium Hydride (Beany) Particles,  
Microscope Magnification - X65

TABLE II  
MIX VISCOSITY AND PROPELLANT DENSITY VALUES FOR BEANY LOTS B464-B478

Lot	As Received		After Grinding		After Air Roasting (b)	
	Mix Viscosity (a)	Propellant Density (% of Theoretical)	Mix Viscosity (c)	Propellant Density	Mix Viscosity (c)	Propellant Density
B464	>500	---	>500	91.5	>500	99.5
B465-6	>500	99.9	480/390	87.6	280/248	97.2
B467-8	>500	---	310/250	92.5	258/220	97.4
B469	>500	99.7	220/190	92.3	168/152	100.2
B470	>500	---	240/208	90.2	240/204	97.6
B471	>500	96.3	>500/442	86.5	>500/395	99.3
B472-3	>500	82.6	>500	80.3	>500/345	99.1
B474	280/140	91.5	250/190	91.9	230/185	98.7
B475	290/180	99.6	240/160	91.8	205/130	>98.0
B476	>500	94.3	>500	91.1	380/240	99.5
B477	>500/460	96.4	360/220	95.7	240/180	99.9
B478	460/260	98.8	260/180	91.9	335/205	98.0

(a) Viscosity values are direct-scale readings, Brookfield Viscometer, T-bar E, 20 rpm, 0 to 500 scale. Where two figures are given, the higher is a Helipath value, the lower a fixed-position reading. Because of mix thixotropy and the use of the small T-bar at high rpm, conversion to cps units would not be valid.

(b) Lots B464 and B471 - B478 were passivated by roasting in air 72 hours at 110°C. The others were roasted only 24 hours.

(c) Mix viscosity values after grinding should not be compared with those after roasting because the latter mixes used a higher mixer speed. Previously, air roasting was found to cause a slight increase in mix viscosities.

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TABLE III  
ANALYTICAL DATA FOR BEANY PRODUCTION SAMPLES (ETHYL DATA)

Lot No.	B464	B465-6	B467-8	B469	B470	B471	B472-3	B474	B475	B476	B477	B478
Total carbon	0.88	1.30	2.62	1.89	---	1.72	1.89	1.16	1.50	1.06	1.37	---
Total hydrogen	17.75	17.26	17.34	17.71	---	17.72	17.25	17.58	17.92	17.56	17.56	---
Purity (% BeH <sub>2</sub> )	96.4	94.7	93.3	95.8	93.9	94.9	93.5	95.7	96.8	95.7	95.9	(95.4)
Beryllium metal	<1.0	<1.0	1.7	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	<1.0	---
Beryllium chloride	---	---	---	---	---	0.66	0.34	0.13	---	---	---	---
Beryllium alkoxides	---	---	---	---	---	0.17	0.08	0.04	---	---	---	---
Beryllium Alkyls	---	---	---	---	---	---	---	---	---	---	---	---
Diethyl	0.2	1.0	2.2	2.3	2.9	1.1	1.0	---	---	---	---	---
Dipropyl	0.0	0.1	0.2	0.1	0.2	0.1	0.1	---	---	---	---	---
Dibutyl	0.9	0.6	0.8	0.6	1.4	1.2	1.8	---	---	---	---	---
True density, g/cc	---	---	---	---	---	0.62	0.61	0.64	0.63	0.65	0.65	0.63
Bulk density, g/cc	---	---	---	---	---	0.31	0.31	0.35	0.37	0.33	0.32	0.34

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Passivation was carried out by roasting the ground materials in air at 110°C for 24 to 72 hours, which raised propellant densities to 97 percent or higher.

b. Evaluation of Continuous Process Beryllium Hydride (BC Lots)

Eight samples from Ethyl Corporation's bench scale continuous reactor have been received. The analytical data (Table IV), by comparison with standard Beany, indicate a 2 to 7 percent lower purity and substantially lower bulk density (Beany ~0.34 g/cc, BC ~0.20 g/cc). Photomicrographs (Figure 2) show that the BC lots consist of agglomerates of much finer particles than those of which Beany is composed. Consequently, much higher mix viscosities were expected. With the standard check-out mixer, none of these lots could be incorporated in the LPC 1032B formulation (15 percent LMH-2, Table I). However, by modifying the mixer to provide a high shear action (vibrating mix blade), it was found possible to incorporate lot BC 83 at the 14.7 percent level (propellant 035-10, Table I) corresponding to a volumetric solids loading (VSL) of 53.7 percent. The viscosity was off-scale on the Brookfield and the mix would not flow without vibration. The agglomerates of lot BC 83 appeared microscopically to consist of larger subparticles than those of the other lots corresponding to the observed lower mix viscosity. Because of its low purity (88.2 percent), no effort was made to optimize its processibility by grinding.

The higher purity lots could not be incorporated in propellant 035-10. However, since the continuous process material represents a potential cost reduction and may burn more efficiently than Beany because of its smaller basic particle size, a motor firing test would be highly desirable. In an effort to provide a castable formulation, the BC lots of 90 percent or higher purity were blended and ground by ball milling for ten minutes. When evaluated in the inherently low viscosity TNEOC system (035-10A, Table I), the BC blend was castable with vibration at 17.5 percent LMH-2. A sufficient quantity of the blend is being processed to provide a 1.5-pound test grain of the 1032-IV (TNEOC) formulation which has an LMH-2 content of 18.8 percent.

c. Task I - Evaluation of Crystalline Beryllium Hydride (Ethylene)

Two 1.5-pound motors of LPC 1032 containing Ethylene were fired. The pressure traces were distinctly dome shaped and had an undesirably slow pressure drop during burn out. These effects are believed caused by grain porosity which was evident in the x-rays before firing. However, the grains burned without any serious malfunction. The data are listed in Table V.

A direct comparison between the Ethylene motors, and the Beane control motors is not possible for the following reasons:

- The Ethylene grains were fired at significantly lower chamber pressures where both theoretical  $I_{sp}$  and efficiency are lower.

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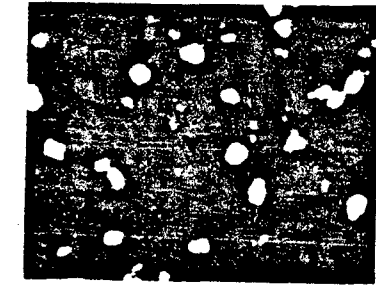
TABLE IV  
ANALYTICAL DATA FOR CONTINUOUS PROCESS BEANY (ETHYL DATA)

<u>Lot No.</u>	<u>BC51</u>	<u>BC56</u>	<u>BC61</u>	<u>BC62</u>	<u>BC80</u>	<u>BC81</u>	<u>BC82</u>	<u>BC83</u>
Purity (% BeH <sub>2</sub> )	93.5	93.6	88.9	93.8	92.1	93.9	90.0	88.2
Beryllium metal	1.0	2.3	---	---	1.0	1.0	1.0	1.0
Beryllium alkoxides	0.04	---	---	---	0.05	0.26	0.67	0.64
Beryllium alkyls	---	1.4	1.7	---	---	---	---	---
Diethyl	---	---	---	---	1.08	0.76	0.90	0.82
Dipropyl	---	---	---	---	0.11	0.12	0.19	0.17
Dibutyl	---	---	---	---	0.84	1.04	1.88	1.44
Total oxygen	6.2	3.3	6.2	---	---	---	---	---
True density, g/cc	---	---	---	---	0.64	0.65	0.66	0.67
Bulk density, g/cc	---	---	---	---	0.15	0.18	0.18	0.20

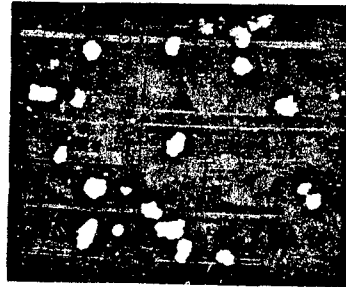
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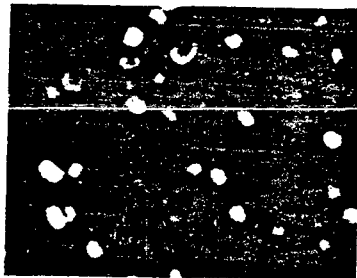




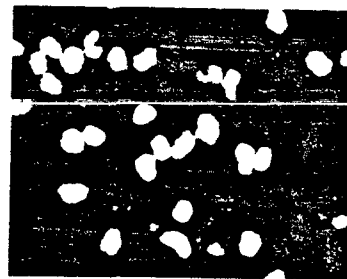
BC62



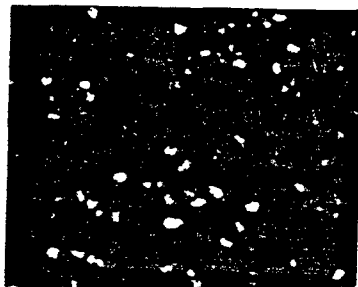
BC81



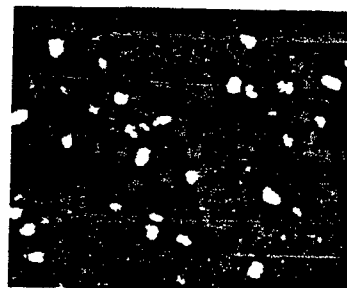
BC56



BC80



Lot BC51



BC61

Figure 2 Continuous Process Amorphous Beryllium Hydride Particles, Microscope Magnification - X65

- The shape of the Ethylene pressure traces makes the average  $P_c$  non-representative of actual firing conditions.
- Particle size of the Ethylene was much larger than that of the Beany.
- Purity of the Ethylene was about 6 percent lower than that of the Beany which would lower theoretical impulse of the Ethylene about 3 seconds.

Additional testing is necessary to establish relative differences, if any, with certainty.

TABLE V  
FIRING TEST DATA, 1.5-POUND MOTORS

Grain No.	Propellant	$P_c$ (ta)	$I_{sp1000}$ (ta)	$I_{sp1000}$
246	1032B (Ethylene)	878	265.1	~300
248	1032B (Ethylene)	763	259.5	~300
257	1032B (Beany)	1048	274.1	303.3
243	1032B (Beany)	1077	272.0	303.3

d. Task I - Surface Area Measurement

Because of suspected effects of Beany specific surface on burning rate and combustion efficiency, an investigation was begun on a method for surface area determination of LMH-2 using a BET-krypton adsorption technique. The method involves a dynamic sorption principle with the Perkin-Elmer-Shell Sorptometer (Model 212C, Perkin-Elmer Corporation, Norwalk, Conn.) with helium and krypton as the carrier and adsorbate gases, respectively. A limited amount of work reported by Wise and Lee (Ref. 2) indicated that surface areas of less than 1.0 sq. meter/gram could be measured with this technique. Using a twofold increased detector current and sorptometer blended concentrations of krypton between 0.025 and 0.057 percent, linear (4 point) BET plots were obtained. From these plots the following specific surface areas were calculated:

$S_s$  ( $m^2/g$ )

	LMH-2 Lot 79	LMH-2 Lot 79 (After 40 min of ball milling)
1	1.269	2.004
2	1.343	1.983
AVE	1.306	1.994
$\sigma$	0.037	0.008

**e. Task I - NF<sub>2</sub> Binder Systems**

Renewed effort was placed on the PBEP/TVOPA binder system cured with triphenylmethane triisocyanate (Quarterly Report No. 716-Q-4). The previous work had resulted in a formulation considered suitable for preparing a grain for test firing based on cures obtained with PBEP lot 9557-80. However, it was found that the cure could not be duplicated with lot 9557-90. Unfortunately, the earlier cures had not been monitored by infrared and no comparisons could be made between the two lots, as used, to determine whether there were significant differences in structure or purity.

Infrared spectra of the binder formulation during attempted cures with the new lot showed that:

- the reaction was not being adequately accelerated by the catalyst FEAA.
- the reaction did not go to completion in 48 hours at 60°C; both hydroxyl and isocyanate absorbance were still evident.

Visual inspection indicated that the cure was non-homogeneous; the mixes contained small lumps of gel surrounding what appeared to be particles of undissolved FEAA. Evidently the catalyst was being deactivated and/or isolated by encapsulation.

Two approaches were tried to improve the cure. First, the PBEP/TVOPA solution in methylene chloride was shaken with sodium bicarbonate, sodium fluoride, and anhydrous magnesium sulfate to remove acidic constituents and water. Material so treated showed an increased reaction rate, but did not cure in 24 hours at 60°C. Second, to obtain a more uniform and finely divided distribution of FEAA, the catalyst was deposited from methylene chloride solution on the AP. Finally, a cure was obtained with FEAA coated AP in a mix with the treated PBEP and reproducibility in propellant mixes was established. A propellant grain of formulation 035-8 (Table I) is being prepared for a 75-gm motor firing test.

**f. Propellant Surveillance Data (Crack Test Samples)**

Determination of the shelflife of crack test samples of LPC-1032B have been in progress at 130°F and 140°F. The samples maintained at 140°F developed cracks sometime after 76 days. Cracking is determined by x-ray. The samples held at 130°F are still intact after 160 days and the surveillance is continuing. Pertinent data with regard to the composition of the test specimens and the results to date of the surveillance tests are given in Table VI.

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TABLE VI  
SURVEILLANCE TESTS OF LPC-1032B

<u>Plasticizer</u>	<u>Stabilizers</u>	<u>Result</u>
LPC-synthesized NIBTN	1% 2-NDPA 1% Phloroglucinol	Cracked, 76-104 days/140°F
LPC-synthesized NIBTN	1% 2-NDPA 1% Resorcinol	Cracked, 76-104 days/140°F
Trojan NIBTN, column treated	1% 2-NDPA 1% Resorcinol	Cracked, 130-167 days/130°F
TMETN analog	1% 2-NDPA	Cracked, 130-167 days/130°F
Trojan NIBTN, column treated	2% 2-NDPA 1% Resorcinol	No cracks, 165 days/130°F
Trojan NIBTN, column treated	1% 2-NDPA 2% Resorcinol	No cracks, 167 days/130°F
LPC-synthesized NIBTN	1% 2-NDPA 1% Resorcinol	No cracks, 141 days/130°F

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**SECTION III****TASK II - LIGHT METAL HYDRIDE PROPELLANT SHELF LIFE****(C) 1. INTRODUCTION AND SUMMARY**

(C) The use of solid propellant ingredients, such as aluminum hydride, which exhibits a measurable rate of gas generation within the operational temperature range of a propellant (motor) creates the problem of internal gas pressure buildup. If this pressure becomes excessive, the grains will likely fail by developing excessive porosity or cracks.

(U) More precisely, grain failure in such systems is the consequence of an imbalance between gas generation rates and gas dissipation rates, the latter being highly dependent upon volumetric solid loading, grain size, and grain geometry. Because of this dependency, there are no simple means for predicting motor shelflife by extrapolation of laboratory surveillance test data. Instead, such data extrapolation must rely on the use of a complex mathematical model, and requires precise information on gas solubilities in the binder, gas diffusion and gas generation rates, in addition to data on grain internal stress concentrations.

(C) Under this program the equations were developed and solved which define time dependent internal gas pressure as a function of light metal hydride decomposition rate (exponential temperature dependent kinetics), propellant parameters (gas solubility, gas diffusion rates), and grain parameters (configuration, web thickness). As a second step, the necessary data were obtained on gas generation rates, gas solubility, and gas diffusion rates, using various grades of aluminum hydride (standard material, magnesium stabilized material) and various propellant systems. In parallel steps, a propellant surveillance program was conducted to provide experimental verification of the postulate that grain failure will occur at that point in time where grain internal gas pressure starts to exceed propellant stress capability. Finally, the results were applied to predicting large motor shelflife and/or in defining minimum necessary material ( $\text{AlH}_3$ ) thermal stability for attaining a given shelflife (time/temperature) with a given size grain (motor).

(C) Results of this effort are highlighted as follows:

- (C) • Measurements were performed upon LPC aluminum hydride CMDB propellants (standard, not crosslinked), and propellants received from the Hercules Powder Company (crosslinked,  $\text{AlH}_3$  CMDB system) and the United Technology Center ( $\text{AlH}_3$  nitrate-polyester system). These various propellants had been processed using an identical lot of standard unstabilized aluminum hydride. In addition, stabilized forms of aluminum hydride (magnesium doped, magnesium doped DPA treated) were used

and evaluated in the LPC CMDB propellant.<sup>2</sup> None of the  $\text{AlH}_3$  samples, however, were representative of the most stable material now available.<sup>3</sup>

- (U) • A semi-quantitative (factor of 2-3) agreement was obtained between calculated (predicted) time-to-failure and time-to-failure determined experimentally using small cylindrical surveillance samples stored at 75° F, 100° F, and 115° F.

Since the calculated (predicted) time-to-failure is based upon an estimate of propellant internal stress capability, to be determined using very low strain rates, such initial agreement between prediction and test data can be considered satisfactory; as a result, the established equations and data can be used for arriving at meaningful estimates of larger grain (motor) shelf-life with a given grade (stability) hydride.

- (C) • An area which requires further analysis involves the failure modes. In aluminum hydride-fueled standard CMDB propellants (e. g. , LPC system) failure is indicated by the appearance of micro-cracks; this process may involve only a localized increase in propellant volume (decrease in density). Failure in aluminum hydride-fueled crosslinked CMDB propellants (Hercules), or the nitrate-polyurethane propellant (UTC) is characterized by the development of increasing porosity (swelling); this is a process which occurs gradually, especially at low temperature (e. g. , 75° F), making it more difficult to define time-to-failure. These latter propellants also will develop cracks, but at a later time, and not necessarily by the same physical mechanism as the non-crosslinked CMDB systems.
- (C) • In spite of these remaining uncertainties the statement can be made that a distinct improvement in  $\text{AlH}_3$  thermal stability above that of the materials employed here is required to permit the use of this material in large solid propellant grains. As an example, a 10-fold improvement in thermal stability over the stability of the current pilot plant magnesium doped material in

---

(U)<sup>2</sup> The cooperation received from the Allegany Ballistic Laboratory, the United Technology Center, and the Dow Chemical Company is gratefully acknowledged.

(C)<sup>3</sup> The unstabilized and Mg-doped materials actually employed were stable to the extent of ~5 and ~10 days for 1-percent decomposition at 60° C. In a recent report (FS-1S-66, October 66) Dow claims the following values for more optimized material: (a) Mg-doped, 15-25 days, (b) Mg-doped and DPA, 50-65 days, (c) Mg-doped + cold aging, 85-100 days. A more pertinent comparison, however, is the time required for 0.1-percent decomposition of the  $\text{AlH}_3$  in the propellants of interest and at the temperatures of interest; such a comparison is not now available for (a), (b), and (c).

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the region below 0.1-percent decomposition will be necessary to assure a one year shelflife for a 12-inch thick (web) grain stored at 75°F, and additional improvements are mandatory for storage temperatures of 100-120°F<sup>3</sup>.

(U) 2. THEORY OF GAS GENERATION-DIFFUSION IN RELATION TO PROPELLANT SHELF LIFE

a. Qualitative Description of Process

It is assumed first that the rate of gas production is effectively uniform within the system and is not so high that the gas does not have time to dissolve in the binder---at least until its solubility limit is reached. At any propellant surface exposed to the atmosphere, the dissolved gas is assumed to evaporate immediately; thus, the gas concentration at exposed surfaces is always effectively zero. Consequently, a dissolved gas concentration gradient is established between exposed surfaces and the interior, leading to diffusion of dissolved gas to such surfaces. It is assumed further that the geometry is such that the concentration gradient and hence the diffusion process are one dimensional, e. g., surface loss from the ends of a cylinder is negligible either because the cylinder has a large length-to-radius ratio or because the ends are sealed.

On the basis of this model, differential equations may be set up for the combined gas generation-diffusion process in systems of different geometry.<sup>4</sup> Solution of these equations yields the concentration of dissolved gas as a function of time, geometry, gas generation rate, and gas diffusion coefficient. In conjunction with experimental values of the parameters and with shelflife data for properly designed laboratory specimens, these equations permit extrapolation to the shelflife of other geometries.

b. Quantitative Description

Gas generation-diffusion equations have been derived for several geometries. These have been discussed in detail previously (Ref. 1) and only one such equation is presented here by way of example. For a system of length  $l$  wherein gas is lost only at one end and diffusion therefore occurs from  $x = 0$  to  $x = l$ :

$$\frac{2 D c(x, t)}{v_d} = (l^2 - x^2) - \frac{32 l^2}{\pi^3} \sum_{n=0}^{\infty} \frac{l}{(2n+1)^3} e^{-\frac{\pi^2 (2n+1)^2 D t}{4 l^2}} \sin \left[ \frac{(2n+1)\pi}{2} \cdot \frac{(l+x)}{l} \right] \quad (1)$$

<sup>4</sup>Similar relationships have been reported by Esso for the case of plasticizer loss by diffusion-evaporation (Ref. 2). British workers have treated the gas generation-diffusion problem for slowly decomposing double-base propellants (Ref. 3).

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where

$c(x, t)$  = concentration of dissolved gas per-unit-volume of propellant (g/cc).

$v_d$  = rate of generation of gas per-unit-volume of propellant (g/cc-sec).

$D$  = diffusion coefficient for dissolved gas in propellant ( $\text{cm}^2/\text{sec}$ ). For inert gases above their critical point in polymers above the glass transition,  $D$  is independent of gas concentration.

In equation (1)  $v_d$  is considered to be independent of time. The more general situation with time dependent generation rate has also been treated and examples of calculated concentrations using experimentally determined  $D$  and  $v_d(t)$  are presented in a subsequent equation.

c. Failure Mechanism (Structural Integrity)

At any given time the concentration of dissolved gas will be greatest where diffusional loss is least effective, e. g., at the case for a case-bonded cylinder with an open core or at the closed end of an end-burning motor. As time passes, the concentration of dissolved gas at any point will increase until the system fails (incipient voids or cracks) or until its rate of gas production becomes exactly balanced by its rate of diffusional loss (steady state). Barring a significant increase in gas generation rate, a system which has been able to attain the steady state should never fail unless long time creep processes taking place under the stress of the gas pressure ultimately lead to failure or unless aging itself leads to degradation of mechanical properties.

Since the failure locus and mechanism are not known a priori, the failure criterion must remain relatively undefined at present. Failure obviously will be initiated when and if the pressure exerted by dissolved gas exceeds atmospheric pressure plus some localized stress capability. The more soluble the gas in a given system, the lower will be the gas pressure and the less likely will be failure, other factors being equal. If the stress capability within the system were uniform, the presence of dissolved gas should cause failure preferentially where the gas concentration is greatest, e. g., in the region of the case or liner for a case-bonded, internal-burning motor. Obviously the stress capability will not be uniform however; the propellant-liner bond and/or the binder-solids bond may be weak and a case-bonded system may have cure shrinkage and thermally induced stresses. Also, it is entirely conceivable that failure may be initiated within the binder phase itself, in which case the controlling factor may be the binder modulus.

It may be noted that a reciprocity exists between gas concentration and pressure (or stress) through Henry's law,  $c=SP=S\sigma$ .  $S$  may be thought of as the maximum permissible concentration of dissolved gas at one atmosphere pressure and  $\sigma$  as the internal stress exerted by the gas upon the



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propellant and the pressure (stress) exerted in turn by the propellant upon the gas. Whatever the failure initiation mechanism, if it requires a stress greater than 14.7 psi, the permissible gas concentration can become correspondingly greater than S.

While the above really considers conditions for initiation of void formation (microscopic failure) Lawson has treated the question of the critical pressure within a gas-filled spherical void (bubble) necessary to rupture the bubble (macroscopic failure). (Ref. 4.) He arrives at equation 2,

$$P \text{ (critical)} \approx \frac{2 E \phi}{1 + 2 \phi} \quad (2)$$

where E and  $\phi$  are the tensile modulus and the elongation at break of the binder measured of course at strain rates corresponding to those during growth of the spherical void. For any practical system of acceptable shelf-life the strain rates involved must of necessity be very small. After rupture of the bubble, stress concentration points will undoubtedly exist and favor growth of the rupture point---probably at lower pressures than were required for the rupture itself.

The presence of only a few microscopic voids between the time of "microscopic" failure and "macroscopic" failure should not significantly affect the overall gas solubility and diffusion rate. Hence, the above critical pressure should correspond to a gas concentration calculable with the generation-diffusion equations. If, on the other hand, appreciable porosity is produced before "macroscopic" failure occurs, the effective gas diffusion rate and solubility may be significantly increased, and the present generation-diffusion equations will not be applicable much beyond the "microscopic" failure time.

Thus, our ability at present to make accurate predictions of shelflife will be somewhat dependent upon the details of the "failure" process and therefore upon the nature of the propellant. For example, because of the relatively granular nature of the slurry-cast double-base binders (poorly solvated nitrocellulose particles), such systems may be expected to rupture rather easily and quickly once initial, localized microscopic void formation has occurred. In contrast, a crosslinked binder, particularly a completely solvated one, should be much more capable of withstanding the presence and growth of voids without actually rupturing. In terms of equation 2, the latter system may possess a larger modulus and larger elongation at rupture than would the former system.

### (C) 3. SYSTEMS STUDIED

The LPC, ABL double-base binder, and UTC polyester binder propellant systems have been studied. Formulations for these systems are given in Table VII, along with those of Al analog propellants employed in the diffusion and solubility measurements.

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TABLE VII  
LMH-1 SURVEILLANCE PROPELLANT FORMULATIONS (Volume %)

	<u>LPC- 1018B-C</u>	<u>LPC- A23-06</u>	<u>LPC- A23-06C</u>	<u>UTP- 6814</u>	<u>UTP- 6646</u>	<u>ABL- FHA</u>	<u>ABL- Control</u>
PNC	15.9	22.0	22.0			8.0	8.0
TMETN	29.9	29.3	29.3	15.1	15.1		
TEGDN	20.3	22.1	22.1			4.1	4.1
Stabilizer	1.6	1.9	1.9			0.6	0.6
Al			24.8		27.4		25.8
AP	32.4			40.2	39.8	17.5	17.5
LMH-1		24.8		27.0		25.8	
HX-735				15.2	15.2		
MAPO				1.6	1.6		
Epon 812				1.0	1.0		
HMX						13.1	13.1
NG						27.4	27.4
BDNPA						2.8	2.8
PGA-TDI						0.7	0.7
Volume % Polymer in Binder	30			55		19	

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Four samples of LMH-1 have been included in the investigation (See Table VIII):

- Blend 970131. For comparisons of stability, a blend of several pilot plant lots of unstabilized (non-doped), macrocrystalline LMH-1. This was acrylonitrile treated before use.
- Mg-doped, Lot 03296. This also was acrylonitrile-treated.
- Mg-doped, Lot 07146. This was not acrylonitrile-treated.
- Mg-doped, DPA-treated, Lot 07146. This was not acrylonitrile-treated.

(C) 4. GAS GENERATION RATE (LMH-1 Stability)

a. Experimental Procedure

A technique has been developed wherein the samples (LMH-1 by itself or finely chopped in propellant) are sealed in H<sub>2</sub>-tight metal tubes which are connected to a thermal conductivity detector through a valving arrangement. After permitting the H<sub>2</sub> to collect in the thermostatted sample tube for known periods, the proper valves are opened, thus allowing a carrier gas (argon) to flush the collected H<sub>2</sub> into the detector. As presently set up six samples can be studied simultaneously. A bypass loop around the valve assembly permits a continuous flow of carrier gas through the detector; it also contains valves with calibrated loops for calibration purposes. This apparatus is capable of being automated. Each sample tube is checked for tightness with a He leak detector before being placed in an oven and connected to the valve assembly. No significant pressure or flow effects are observed unless collection times are extended to the point where an appreciable H<sub>2</sub> pressure has been built up. With the LMH-1 sample (blend 97-131, a blend of Dow pilot-plant lots) for example, collection periods must be limited to only one or two hours at 140°F during the peak of the gas generation rate-versus-time curve. In general, the technique appears to be very satisfactory; its only serious drawbacks being the length of time required to purge the sample tubes completely of H<sub>2</sub> (up to one hour) and the consequent slow tailing-off of the detector curve plus limitations in sensitivity to be pointed out subsequently.

b. Results

The data results are presented in Figures 3, 4, and 5. The actual curves shown in the figures have been calculated using parameters obtained by visually fitting the data (on an appropriate logarithmic plot) to the equation

$$v_d = v_d^0 + bte^{kt} \quad (3)$$

where  $v_d$  is the gas generation rate in ul H<sub>2</sub>-per-g of LMH-1 per hour,  $t$  is

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TABLE VIII  
COMPARISON OF STABILITIES OF VARIOUS  $\text{AlH}_3$  SAMPLES

Material	Days for 1% Decomposition at 60°C (140°F)	Days for 1% Decomposition at 60°C (140°F)	Days for 1% Decomposition at 46°C (115°F)
A. Unstabilized blend			
(1) Neat (LPC data)	5 1/2 (a)	2 1/2 (a)	
(2) Neat (Dow data)	5 (b)	2	
(3) In LPC propellant (LPC data)	4 1/2 (a)	1 1/2 (a)	6 1/2 (a)
B. Mg-doped			
(1) In LPC propellant (Lot 03296)			35 (a)
C. Dow data for range of samples			
(1) Mg-doped	15-25 (c)		
(2) Mg-doped + DPA	50-65 (c)		
(3) Mg-doped + cold aging	85-100 (c)		

- (a) Calculated from parameters of Table X.
- (b) Personal communication from Dow Chemical.
- (c) Dow, FS-15-66, Oct 66, Figure 3.

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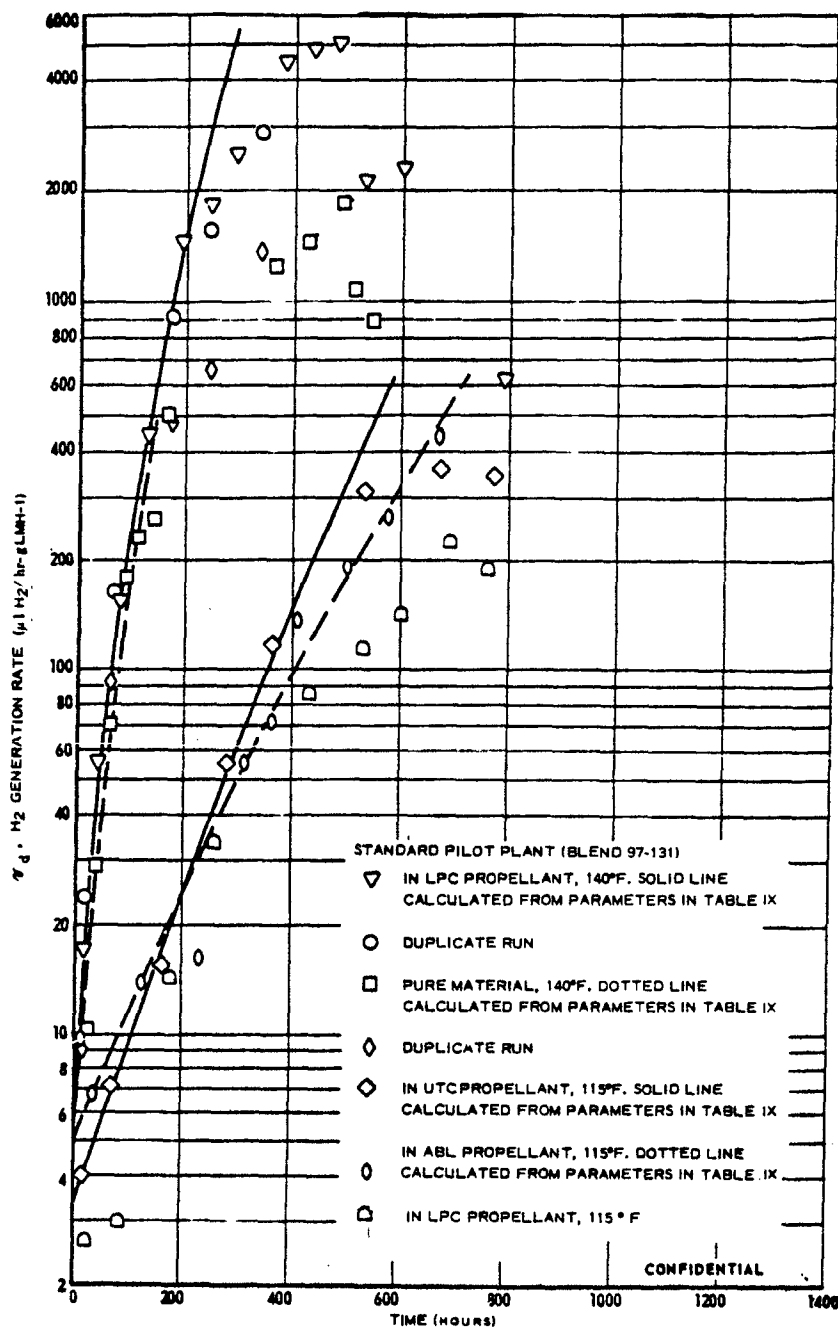


Figure 3  $H_2$  Generation Rate

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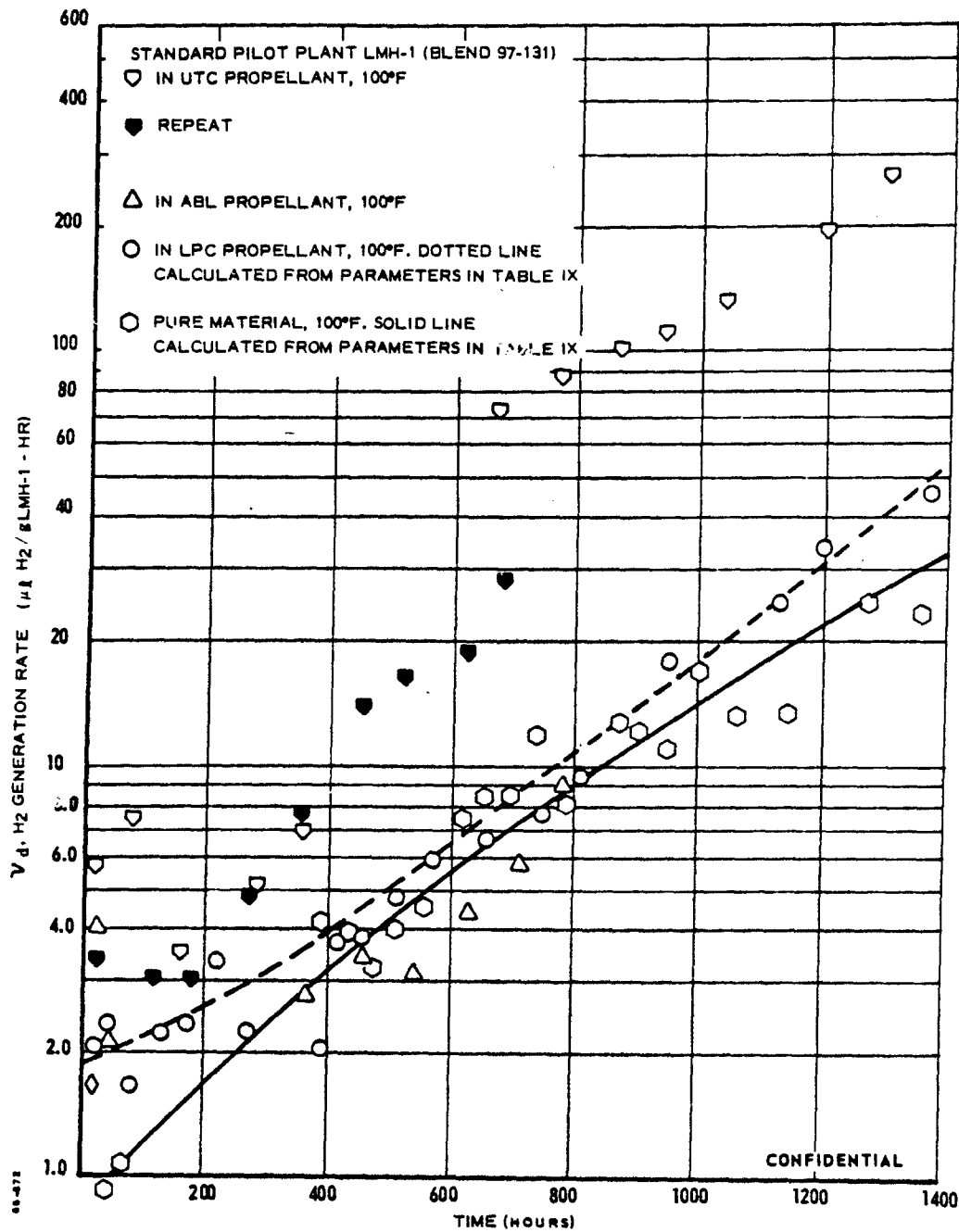


Figure 4  $H_2$  Generation Rate

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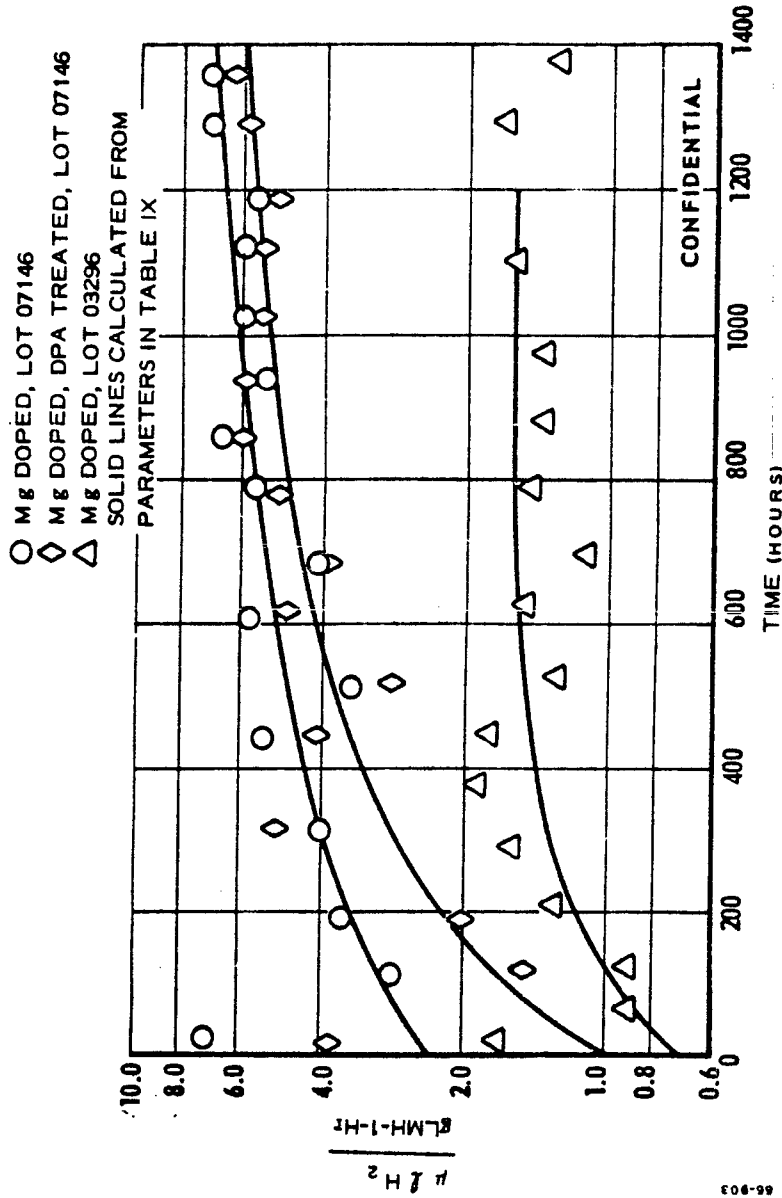


Figure 5 H<sub>2</sub> Generation Rate of Stabilized LMH-1 in LPC-A23-06 Propellant at 115°F

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time in hours, and  $v_d^0$ ,  $b$  and  $k$  are constants for a given system and temperature. This equation has no theoretical basis per se but does fit all the data satisfactorily in the region of interest for shelflife (< 1-percent decomposition). It also possesses the additional (and essential) virtue of yielding manageable expressions for the time dependent gas generation-diffusion relationships (c.f., equation (41), Appendix, Reference 1). Integration of equation (3) yields expressions for the percent decomposition versus time. Examples of such calculated curves are given in Figure 6.

The parameters obtained for equation (3) are presented in Table IX. Values for the unstabilized blend are plotted against  $1/T$  ( $^{\circ}K$ ) in Figures 7 and 8 for the purpose of extrapolating to  $75^{\circ}F$ , where the thermal conductivity method is not sufficiently sensitive to permit reasonable measurements. Such an extrapolation obviously is risky and the resulting predicted gas generation rates must be accepted with reservation. Mass spectrometric experiments have been planned to provide direct measurements of generation rate for the unstabilized LMH-1 at  $75^{\circ}F$  and for the stabilized material (see Figure 5) at  $100^{\circ}F$  and  $75^{\circ}F$ .

The observed data scatter is believed to be the result of temperature fluctuations ( $\pm 1/2$  to  $1^{\circ}C$ ) and errors in measuring the integrated thermal conductivity signal during both calibration and actual sample measurements. Variations in the calibration constant are estimated at about  $\pm 4$  percent; assuming a similar error in the samples leads to a total error (aside from temperature effects) of approximately  $\pm 10$  percent. The number of data points, however, do permit an averaging to produce rate-time curves of good accuracy. There seems no doubt, for example, that the two curves for Lot 07146, DPA-treated and untreated (Figure 5) are significantly different.

Satisfactory reproducibility below the 1-percent decomposition range is evidenced by the duplicate runs at  $140^{\circ}F$ , both neat LMH-1 and in LPC propellant (Figure 3), and by the UTC data at  $100^{\circ}F$  (Figure 4). In Figure 6 the calculated percent decomposition curves at  $140^{\circ}F$  agree satisfactorily with the Dow pressure transducer bomb derived values. Table VIII presents a comparison of times to various decomposition for various  $AlH_3$  samples.

In view of the greater gas generation rate observed at  $140^{\circ}F$  (Figure 3) and  $100^{\circ}F$  (Figure 4) for LMH-1 in propellant over that of the neat material, the gas generation rate was measured for control propellant (Al analog) at  $140^{\circ}F$  to rule out interference by DB binder decomposition. The values obtained (expressed per gram of equivalent LMH-1) were all below 1 to 2 percent of the rates for the LMH-1 system during the 500 hours of observation. Moreover, separate gas chromatographic analyses upon the gas generated from the LPC  $AlH_3$  propellant at  $140^{\circ}F$  demonstrated that  $H_2$  constituted > 99 percent of the gas. Finally, LMH-1, both neat and in LPC propellant, was carried to essentially complete decomposition at  $140^{\circ}F$  (~2000 hours), and integration of the measured gas generation rate versus time curves yielded total amounts of  $H_2$  liberated which were equal ( $\pm 10$  to 15 percent) to the theoretical  $H_2$  in the samples. (The lower generation rate



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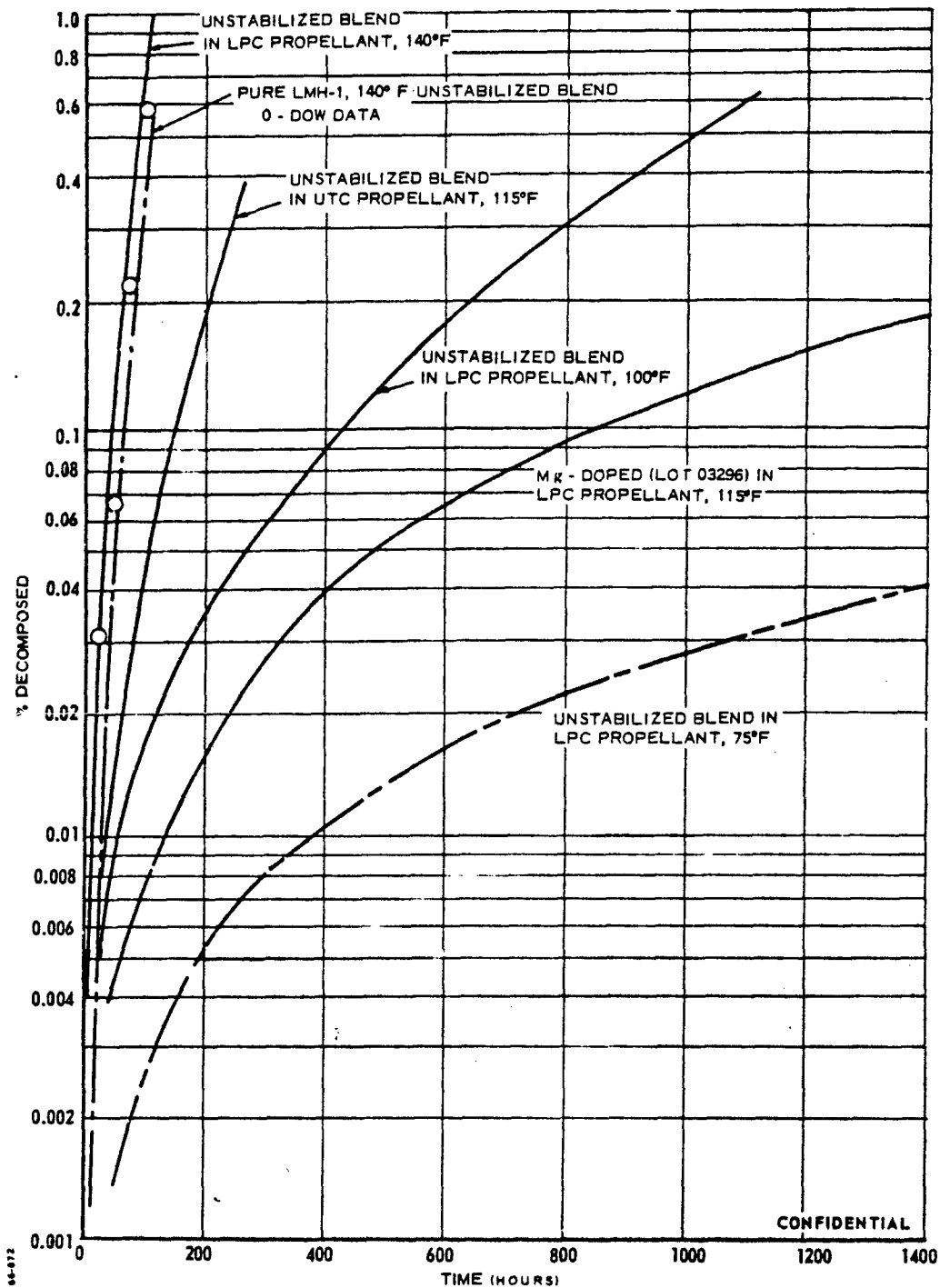


Figure 6 Calculated Percent Decomposition Curves for LMH-1

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TABLE IX  
PARAMETERS FOR GAS GENERATION RATE EQUATION

$$v_d = v_d^0 + bte^{kt} \text{ (}\mu\text{l H}_2\text{/hr-gLMH-l)}$$

Sample	$v_d^0$	b	k
A. Unstabilized blend (97-131)			
(1) Neat, 100°F	0.80	0.0034	0.00137
(2) In LPC-A23-06, 100°F	1.90	0.0022	0.0020
(3) In LPC-A23-06, 115°F	1.7	0.035	0.0035
(4) In LPC-A23-06, 140°F	6.0	0.77	0.0112
(5) In LPC-A23-06, 75°F (Extrapolated from (2), (3) & (4))	0.30	$2.5 \times 10^{-5}$	$5.0 \times 10^{-4}$
(6) In ABL-FHA, 100°F	2.1	$9.5 \times 10^{-4}$	0.0024
(7) In ABL-FHA, 115°F	5.0	0.043	0.0042
(8) In ABL-FHA, 75°F (Extrapolated from (6) & (7))	0.57	$2.0 \times 10^{-5}$	$5.6 \times 10^{-4}$
(9) In UTP-6814, 100°F	2.5	0.0039	0.0036
(10) In UTP-6814, 115°F	3.3	0.035	0.0058
(11) In UTP-6814, 75°F (Extrapolated from (9) & (10))	1.20	$8.0 \times 10^{-6}$	$9.0 \times 10^{-4}$
B. Mg-doped, Lot 03296			
(13) In LPC-A23-06, 115°F	0.70	0.0027	-0.0011
(14) In LPC-A23-06, 100°F (Extrapolated)	0.45	$4.0 \times 10^{-4}$	$-2.4 \times 10^{-4}$
(15) In LPC-A23-06, 75°F (Extrapolated)	0.15	$2.5 \times 10^{-6}$	$-5.4 \times 10^{-5}$
C. Mg-doped, Lot 7146			
(16) In LPC-A23-06, 115°F	2.4	0.0059	$-4.2 \times 10^{-4}$
(17) In LPC-A23-06, 100°F (Extrapolated)	1.5	0.0010	$-2.8 \times 10^{-4}$
(18) In LPC-A23-06, 75°F (Extrapolated)	0.42	$9 \times 10^{-6}$	$-6.0 \times 10^{-5}$
D. Mg-doped, DPA-treated, Lot 07146			
(19) In LPC-A23-06, 115°F	1.0	0.0068	$-4.7 \times 10^{-4}$

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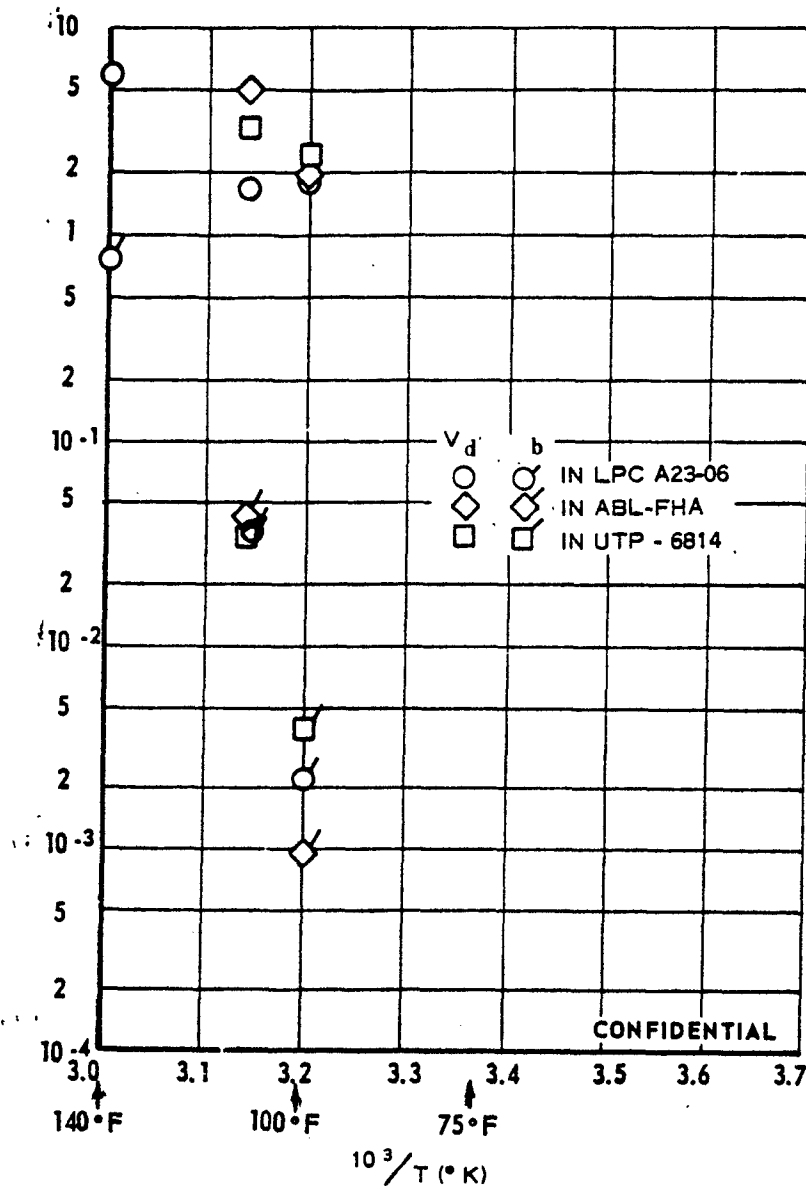


Figure 7 Gas Generation Rate Parameters  $v_d$  and  $b$  for Unstabilized LMH-1

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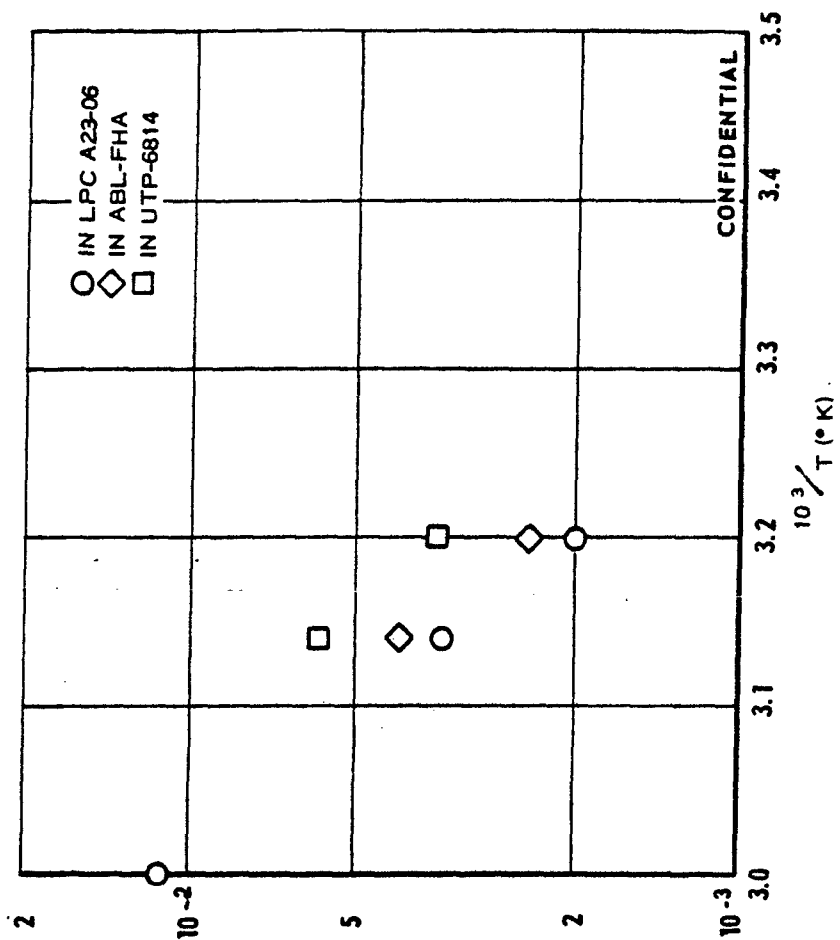


Figure 8 Gas Generation Rate Parameter k for Unstabilized LMH-1

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for the neat material observed during the initial stages was compensated, incidentally, by a shift of the rate curve for the neat material to longer times and by a slower tailing off in the last stages of decomposition).

Originally it had been intended to measure gas generation rates during cure to provide continuous values corresponding to the actual history of surveillance specimens. Unfortunately the sensitivity of the thermal conductivity method proved insufficient because of the inherently low rates during the very first stages of decomposition and because of the necessity to employ thin layers of uncured propellant to void diffusional effects. Zero times for the reported generation rates therefore neglect any cure times. For any really practical LMH-1 systems, i. e., those with relatively long shelflives, the error introduced by ignoring the cure time would be negligible; this condition is not met by all the systems studied here, however.

#### c. Critique of Experimental Technique Used

The experimental technique used (thermoconductivity cell) proved satisfactory for measuring hydride and hydride propellant gas generation rates at temperatures above 90 to 100°F, and without incurring undesirable interferences (e. g., mercury effect associated with Taliani equipment; effect of leaks associated with pressure equipment). However, the method still lacked sensitivity for measuring gas generation rates at 75°F. Thus a more sensitive technique is needed for evaluating material/propellant stability within a temperature range that can be considered to be the lower limit for propellant storage.

### (C) 5. H<sub>2</sub> DIFFUSION CONSTANTS AND SOLUBILITIES

#### (U) a. Experimental Procedure

The apparatus and general method have been described in detail in Reference 1. Briefly, the diffusion coefficient,  $d$ , is obtained by a rate of sorption method while the solubility at one atmosphere of H<sub>2</sub> is obtained from the equilibrium sorption. The apparatus consists of two modified safety (rupture) heads, one of which contains thin propellant discs, while the other contains similar Al discs. After introducing H<sub>2</sub> into the previously evacuated cells, the rate of differential pressure change due to sorption of H<sub>2</sub> by the propellant discs is observed.

#### (C) b. Results

(U) The diffusion coefficients and solubilities (1 atmosphere pressure) determined in the three control (Al analog) propellants are shown in Figure 9. The precision of the  $D$  values is quite good, except perhaps in the ABL propellant where it has not been possible to carry out additional experiments. The scatter in the  $S$  values is somewhat greater. Greater  $D$  and  $S$  in the LPC propellants than in the ABL and UTC systems is due primarily to the lower solids contents of the former (LPC) systems.

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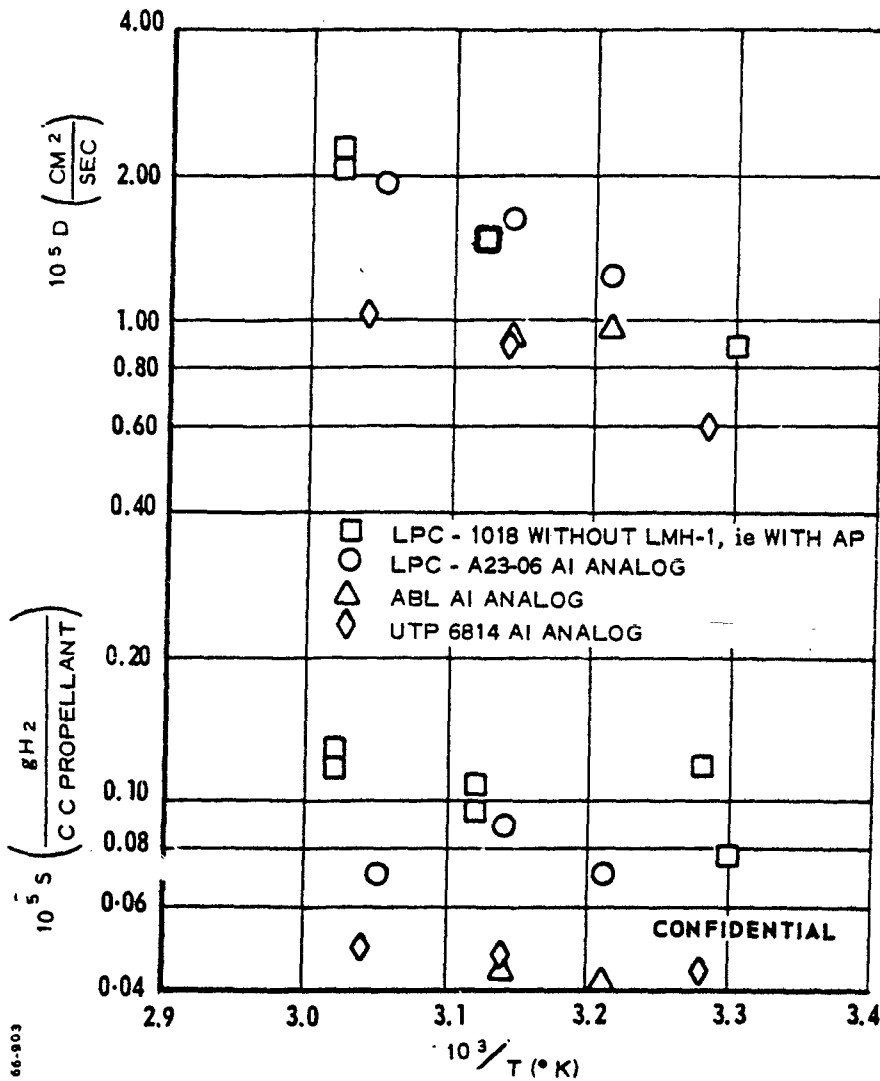


Figure 9 Diffusion Coefficient and Solubility of  $\text{H}_2$  in Propellants

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(C) In Figure 10 both D and S have been divided by  $V_B$ , the volume fraction of binder. In the case of solubility the resultant values should reflect the inherent ability of the various binders to dissolve  $H_2$ , assuming no interaction between solids and  $H_2$  and complete availability of binder. At this juncture it is not apparent why the solubility should be less for nonpolar  $H_2$  in the ABL and LPC-A23-06 binders--or in fact whether the effect is actually real or a reflection of errors in the measurement. In any event these binder solubilities are of the same magnitude as reported for  $H_2$  in polymers, e. g.,  $3 \times 10^{-6} \frac{g H_2 (STP)}{1 atm-cc}$  in poly (vinyl acetate) (Ref. 5) and  $1.3 \times 10^{-5} \frac{g H_2 (STP)}{1 atm-cc}$  in polycarbonate (Ref. 7). Lawson also quotes an estimated solubility for  $N_2$  in cordite of  $4 \times 10^{-6} \frac{g N_2 (STP)}{1 atm-cc}$  (Ref. 4). The activation energy for solution (apparent heat of solution) estimated from Figure 10 is approximately +1 kcal/mole. This is consistent with literature values for non-polar gases in polymers (Refs. 6 and 7).

(U) It appears from Figure 8 that  $D/V_B$  is somewhat greater in the UTC polyester system than in the double-base systems. However,  $D/V_B$  is not itself an adequate measure of the inherent diffusion coefficient in a binder since it does not correct for the action of the solids in producing an effectively greater diffusion path length within the propellant. This problem has been treated by Weissberg (Ref. 8) who obtained the following relationship between the effective (observed) diffusion coefficient D in a porous medium and the diffusion coefficient  $D_0$  in the open regions:

$$D_0 \geq \frac{(1 - 1/2 \ln V_B)}{V_B} D \quad (4)$$

Values of  $D_0$  are shown in Figure 11 and the following comments are warranted.

- (U) • The magnitude of  $D_0$  is quite reasonable, literature values for  $H_2$  diffusion constants in various unplasticized polymers ranging between  $10^{-5}$  and  $10^{-7}$   $cm^2/sec$ . The activation energy for diffusion estimated from all data is 6.6 kcal/mole. This is in good agreement with literature values for  $H_2$  of ~6.5 for natural rubber, 6.6 for neoprene, and 5.7 for poly vinyl acetate, all above their glass transition temperatures. (Ref. 9.)
- (U) • For the two LPC binders  $D_0$  is not influenced by small differences in binder composition, nor is D itself influenced differently by AP or Al.
- (U) •  $D_0$  in the ABL double-base binder apparently is somewhat greater than it is in the LPC binder. This is consistent with the lower ratio of polymer to plasticizer in the ABL binder. (See Table VII.)

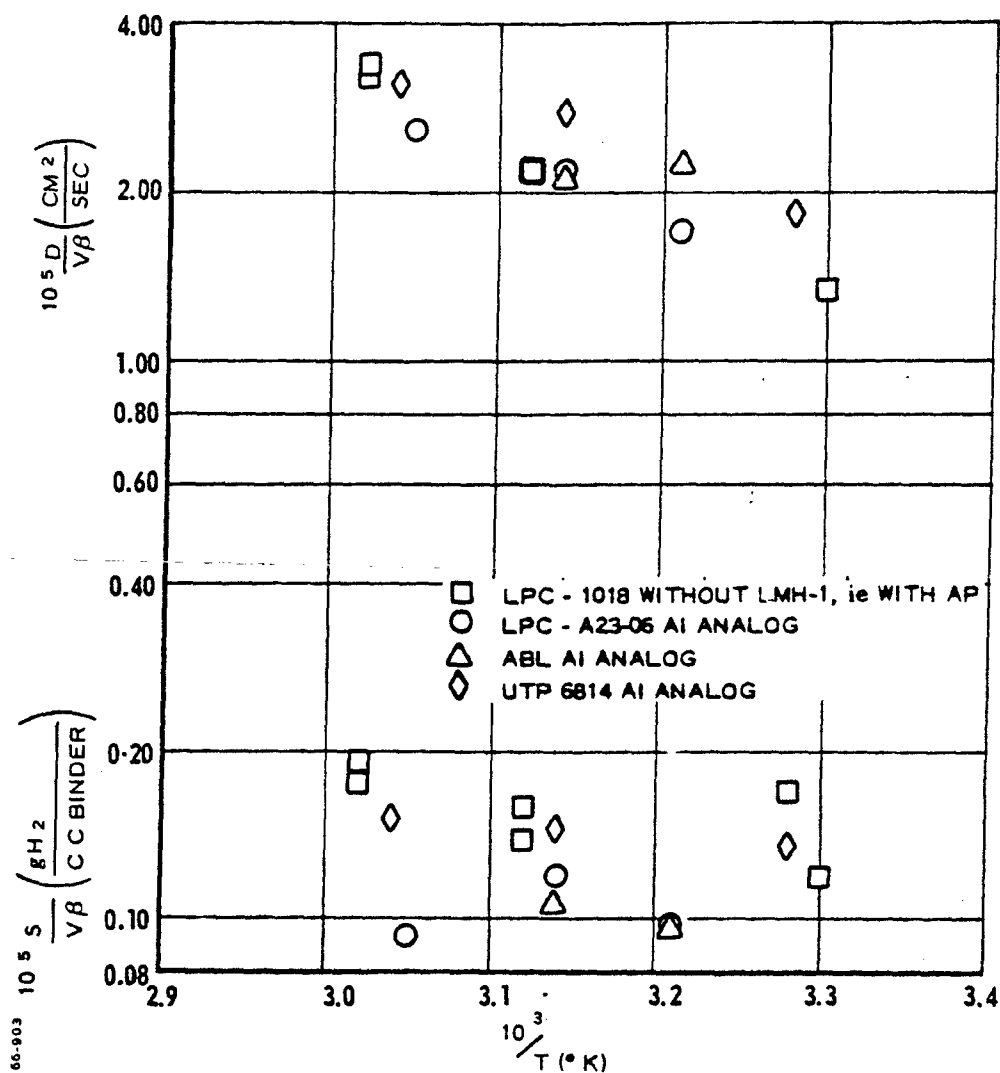


Figure 10 Diffusion Coefficient and Solubility of H<sub>2</sub> per Unit Volume of Binder



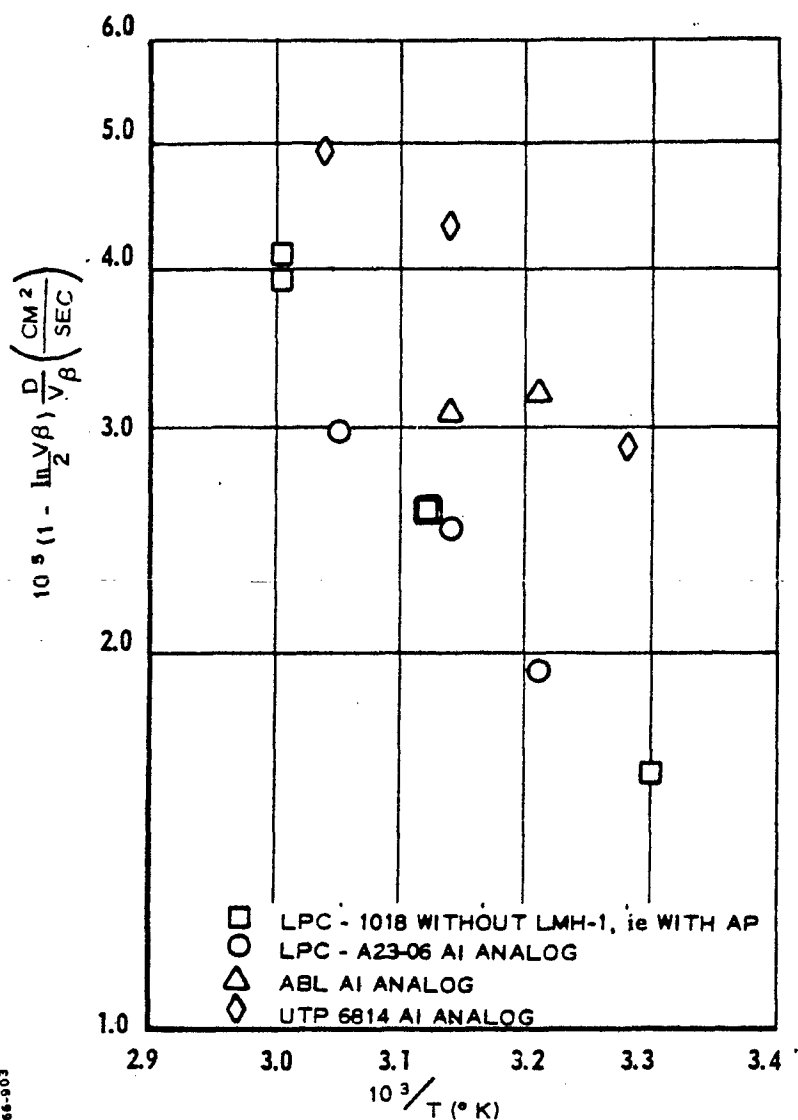


Figure 11 "True" H<sub>2</sub> Diffusion Coefficient in Binder

- (U)      ●  $D_0$  in the UTC polyester binder is significantly (~75 percent) greater than it is in the LPC binder despite the relatively large polymer to plasticizer ratio in the former binder. (See Table VII.) This is undoubtedly a reflection of the inherently greater segmental mobility of a polyester polymer chain relative to that of nitrocellulose.
- (U)      ● The present results certainly are not conclusive proof of the validity of applying equation (4) to these systems but they do lead to qualitatively reasonable observations. Obviously, proof of equation (4) necessitates measurements with a given binder and varying total solids contents.
- (U)      ● The influence of propellant porosity has not been investigated. As indicated previously, porosity could play an important role in modifying the effective diffusion coefficient (and solubility).

(U)      c. Critique of Experimental Technique Used

The method used for measuring gas solubility and gaseous diffusion rates can be considered adequate for the purpose of this program.

(C) 6. LMH-1 PROPELLANT SURVEILLANCE

(U)      a. Experimental Procedures

The following criteria were originally established for surveillance samples:<sup>5</sup>

- Convenient storage of numerous samples under an inert gas purge, using a minimum amount of propellant.
- Diffusion must be one-dimensional (linear, radial) to permit use of the gas generation-diffusion equations.
- Varied diffusion path lengths in a series of samples such that one or more fails in a reasonable time (days to weeks).
- Controlled and variable effect of cure shrinkage and thermally induced stresses.
- Retention of same configuration through cure and storage to simplify application of gas generation-diffusion equations.
- Configuration should be such that a simple vacuum swelling test could provide a routine and sensitive determination of initial void formation.

<sup>5</sup>It will become apparent in the ensuing discussion that this list of criteria would now be considerably modified on the basis of experience gained from the investigation.

On this basis it was decided to employ 1-inch ID and 4-inch ID stainless steel cans, open at one end, as the specimen containers. The 1-inch ID cans were filled to 2, 4, and 6-cm depths and the 4-inch cans to 2.5-cm depth. For every surveillance condition (system and temperature) two or three 1-inch ID specimens of each depth were prepared, whereas only one or two of the 4-inch ID specimens was studied, the larger specimens providing samples which are less affected by thermal stresses and poor liner bonding. Cans were lined, filled with propellant under vacuum, cured, and stored in purged ovens. Periodically the specimens were checked visually by vacuum dilation and by x-ray.

(C) b. Summary of Results

(U) The results of the theoretical analysis (time dependent gas concentration, predicted failure concentrations) and of the surveillance tests (experimental time-to-failure) are summarized in Tables X through XV and in Figures 12 through 18. In these presentations the following information is given:

Tables X through XV

- experimental time-to-failure as a function of storage temperature (75°F, 100°F, 115°F) and sample configuration, relying on X-ray analysis, vacuum swelling tests, and visual observation for defining failure times.
- calculated (predicted) time-to-failure relying upon the model (equation 41, Appendix, Reference 1), and an estimated value for the limiting (failure) gas concentration in the propellants (Section c. below).

Figures 12 through 18 present the same information in graphic form to show the range of failure points along the calculated maximum gas concentration curves.<sup>6</sup>

Figure 19 presents photographs of some of the 115°F surveillance samples containing unstabilized LMH-1. These graphically illustrate the eventual effects which can be produced by the internal gas pressure.

(C) These data show that in the majority of cases, particularly in the most meaningful cases, failure occurred in accordance with the predicted range of limiting gas concentration, i. e.,  $10^{-5}$  to  $10^{-6}$  g H<sub>2</sub>/cc propellant. It implies that the theoretical analysis underlying this approach is correct within the limits to be discussed below, and that the existing model can be used for predicting a time range wherein larger grains (motors) are likely to fail catastrophically, using an AlH<sub>3</sub> material of given thermal stability.

<sup>6</sup>Concentrations are referred to as maximum values because they apply at the bottom of the specimens where the gas concentration must be the greatest.

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TABLE X

SURVEILLANCE DATA FOR ABL-FHA PROPELLANT  
(BLEND 97-131, UNDOPED LMH-1)

Sample 75°F <sup>(b)</sup>	Time to Observe Failure (Hours) <sup>(a)</sup>			
	Vacuum Dilation	X-Ray	Visual	From Failure Envelope(g)
S-6 cm	<240	<240	600-700 <sup>(d)</sup>	150-400
S-4 cm	<240	<240	~1500 <sup>(d)</sup>	170-600
		No apparent change after 650 hours. Horizontal cracks near top at ~1500 hours.		
S-2 cm	<240	<240	>3200	2100-4700
		No change after 3200 hours.		
L-2.5 cm	<240	<240	~1250	320-3300
		No change after 650 hours. Horizontal cracks near top at ~1250 hours.		
Controls	>240	>650	~1250 <sup>(e)</sup>	
<u>115°F<sup>(c)</sup></u>				
S-6 cm	<92	<92	~260 <sup>(f)</sup>	
		Increase in porosity plus some small cracks at 260 hours.		
S-4 cm	<92	<92	~260 <sup>(f)</sup>	
S-2 cm	<92	<92	~330 <sup>(f)</sup>	
L-2.5 cm	<92	<92	~260	
		Badly cracked at 260 hours.		
Controls	>92	>260	>260	

- (a) Samples containing LMH-1 showed positive vacuum swelling and general porosity by X-ray upon arrival at LPC. Density at that time was 96 percent of theoretical.
- (b) Times at 75°F include 10 days at ambient but exclude ~30 days at 0°F prior to receipt at LPC and 92 hour cure at 115°F.
- (c) Times at 115°F include 92 hours cure at 115°F but exclude 10 days at ambient and 30 days at 0°F.
- (d) Doming began and increased very slowly.
- (e) Cracks at top perimeter.
- (f) Doming observed initially and after a few days plug movement out of containers became apparent.
- (g) Figure 13. (Gas generation rate equation in question beyond 3000 hours and calculated concentrations rising too rapidly.)

TABLE XI  
SURVEILLANCE DATA FOR LPC-A23-06 PROPELLANT  
(BLEND 97-131, UNDOPED LMH-1)

Sample <sup>(a)</sup>	Time to Observe Failure (Hours) <sup>(b)(e)</sup>			
	Vacuum Dilation	X-Ray	Visual	From Failure Envelope <sup>(f)</sup>
<u>75°F<sup>(c)</sup></u>				
S-6 cm	139	146	210	200-800
S-4 cm	>816	>624	816	270-2000
S-2 cm	>1300	>4800	>4800	3000-5500
L-2.5 cm	--	>4800	>4800	1800-4300
Controls	>1650	>1650	>4800	
<u>115°F<sup>(d)</sup></u>				
S-6 cm	60-130	60-130	~140	
S-4 cm	60-130	60-130	~140	
S-2 cm	60-130	>200	~140	
L-2.5 cm	60-130	>200	~140	
Controls (A23-06C)	>200	>200	>200	

- (a) "S" samples in stainless steel cans (lined), 1.1-inch ID and designated depth of propellant. Two to three samples of each S size were observed. "L" samples in stainless steel cans (lined), 4-inch ID and designated depth of propellant. One to two L samples observed. Control samples were Al analog propellant in 1.1-inch cans of 2, 4, and 6 cm depth.
- (b) Density after cure was >99 percent of theoretical.
- (c) Times beyond 16-hour cure at 115°F.
- (d) Times include 16-hour cure at 115°F.
- (e) Initial void (crack) formation in S samples generally appeared ~2/3 of radial distance from center. Visual failure observed as cracks at top perimeter and eventual rising of propellant as a plug.
- (f) Figure 12. (Gas generation rate equation in question beyond 3000 hours and calculated concentrations rising too rapidly.)

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TABLE XII  
SURVEILLANCE DATA FOR PROPELLANT UTP-6814  
WITH UNDOPED LMH-1 (BLEND 97-131)

<u>Sample</u> <u>75°F<sup>(b)</sup></u>	<u>Time to Observe Failure (Hours)<sup>(a)</sup></u>			
	<u>Vacuum Dilation</u>	<u>X-Ray</u>	<u>Visual</u>	<u>From Failure Envelope<sup>(f)</sup></u>
S-6 cm	<380	<380 No apparent change by 1300 hours	1770 <sup>(d)</sup>	120-370
S-4 cm	<380	<380 No apparent change by 1300 hours	1770 <sup>(d)</sup>	120-530
S-2 cm	<380	<380 No apparent change by 1300 hours	2040 <sup>(d)</sup>	630-4200
L-2.5 cm	<380	<380 Horizontal cracks between 1300 and 1700 hours	1700 <sup>(d)</sup>	160-3300
Controls (UTP-6646)	>380	>900	>2044	
<u>115°F</u>				
S-6 cm	<72	<96 Increase in porosity and probably some hori- zontal cracking by 170 hours	170 <sup>(e)</sup>	
S-4 cm	<72	<96 Increase in porosity and probably some hori- zontal cracking by 170 hours	170 <sup>(e)</sup>	
S-2 cm	<72	<96 Increase in porosity and probably some hori- zontal cracking by 170 hours	170 <sup>(e)</sup>	
L-2.5 cm	<72	<96 Horizontal cracks by 170 hours	170 <sup>(e)</sup>	
Controls	>72	>170	>550	

- (a) Samples containing LMH-1 showed positive vacuum swelling test and general porosity by X-ray upon arrival at LPC. Density at that time was 97 percent of theoretical.
- (b) Times at 75°F include 16 days at "ambient" prior to receipt at LPC but exclude 72-hour cure at 120°F.
- (c) Times at 115°F include 72-hour cure at 120°F but exclude 16 days at ambient prior to receipt at LPC.
- (d) Doming.
- (e) Doming. Within 72 hours after doming observed, the S-6 and S-4 samples were rising as a plug out of their containers and one of the L samples was badly cracked across and into the center.
- (f) Figure 14. (Gas generation rate equation in question beyond 3000 hours and calculated concentrations rising too rapidly.)

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TABLE XIII  
115°F SURVEILLANCE DATA FOR LPC-A23-06 PROPELLANT  
WITH MG-DOPED LMH-1 (LOT 03296)

Sample	Time to Observe Failure (Hours) <sup>(a)</sup>			
	Vacuum Dilation	X-Ray	Visual <sup>(b)</sup>	From Failure Envelope <sup>(d)</sup>
S-6 cm	~ 100	--	~ 100	55-200
S-4 cm	310	> 480	~ 525	60-340
S-2 cm	400	480	1000-1400	250-> 1000
L-2.5 cm	~ 400	> 3000 <sup>(c)</sup>	~ 525	90-> 1000

- (a) Includes 16-hour cure at 115°F. Density after cure was >99 percent of theoretical.
- (b) Propellant cracking around top perimeter and beginning to rise as a plug.
- (c) Effective diffusion path for center of specimen approximately  $\frac{1}{2}$  of thickness after visual failure occurred at 525 hours. Sample may well now be in steady state.
- (d) Figure 15. The gas generation rate equation would not be valid beyond 1000 hours; hence the uncertainty in the upper limit for the 2 and 2.5 cm.

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TABLE XIV

SURVEILLANCE DATA FOR LPC-A23-06 PROPELLANT  
WITH MG-DOPED LMH-1 (LOT 07146)<sup>(a)</sup>

Sample	Time to Observe Failure (Hours) <sup>(b)</sup>			
	Vacuum Dilation	X-Ray	Visual <sup>(d)</sup>	From Failure Envelope <sup>(e)</sup>
<u>115°F</u>				
Liner A <sup>(c)</sup>				
S-6 cm	<16	<16. No change after 380 hours.	~ 400	20-65
S-4 cm	<16	<16. No change after 380 hours.	~ 500	20-75
S-2 cm	<16	<16. No change after 380 hours.	~1000	20-550
L-2.5 cm	<16	<16. No change after 380 Hours. Vertical cracks observed at 1600 hours.	~ 600	20-160
<u>100°F</u>				
Liner A				
S-6 cm	<16	<16. No change after 380 hours.	~ 700	40-140
S-4 cm	<16	<16. No change after 380 hours.	~ 600	40-180
S-2 cm	<16	<16. No change after 380 hours.	~ 900	70- >2000
L-2.5 cm	<16	<16. No change after 380 hours. Horizontal cracks observed in center after 1600 hours.	>1600	50-2500
Liner B				
S-6 cm	<16	<16. Increase in void size at 1600 hours.	>1600	
S-4 cm	<16	<16. Increase in void size at 1600 hours.	>1600	
S-2 cm	<16	<16. Increase in void size at 1600 hours.	>1600	

(a) Not ADPN treated.

(b) Includes 16-hour cure at 115°F. All samples gave positive vacuum swelling and X-ray immediately after cure. Density-check samples showed >98 percent of theoretical.

(c) Liner A identical to that used in other LPC surveillance samples in this program.

(d) Cracking at top perimeter, followed by rising as a plug.

(e) Figures 16 and 17.



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TABLE XV  
SURVEILLANCE DATA FOR LPC-A23-06 PROPELLANT WITH  
DPA-TREATED AND MG-DOPED LMH-1(LOT 07146)<sup>(a)</sup>

<u>Sample</u>	<u>Vacuum Dilation</u>	<u>X-Ray</u>	<u>Visual</u>
<u>115°F</u>			
Liner A			
S-6 cm	<16	<16. No change after 380 hours.	~ 400
S-4 cm	<16	<16. No change after 380 hours.	~ 400
S-2 cm	<16	<16. No change after 380 hours.	~ 400
L-2.5 cm	<16	<16. Horizontal cracks near bottom at ~400 hours.	~ 400
<u>100°F</u>			
Liner A			
S-6 cm	<16	<16. No change after 380 hours.	~ 600
S-4 cm	<16	<16. No change after 380 hours.	~ 600
S-2 cm	<16	<16. Horizontal and vertical cracks observed near bottom after 1600 hours.	>1600
L-2.5 cm	<16	<16. Horizontal cracks observed near bottom after 1600 hours.	~ 500
Liner B			
S-6 cm		<16. Increase in void size after ~1600 hours.	>1600
S-4 cm		<16. Increase in void size after ~1600 hours.	>1600
S-2 cm		<16. Increase in void size after ~1600 hours.	>1600

(a) See explanatory notes in Table XV.

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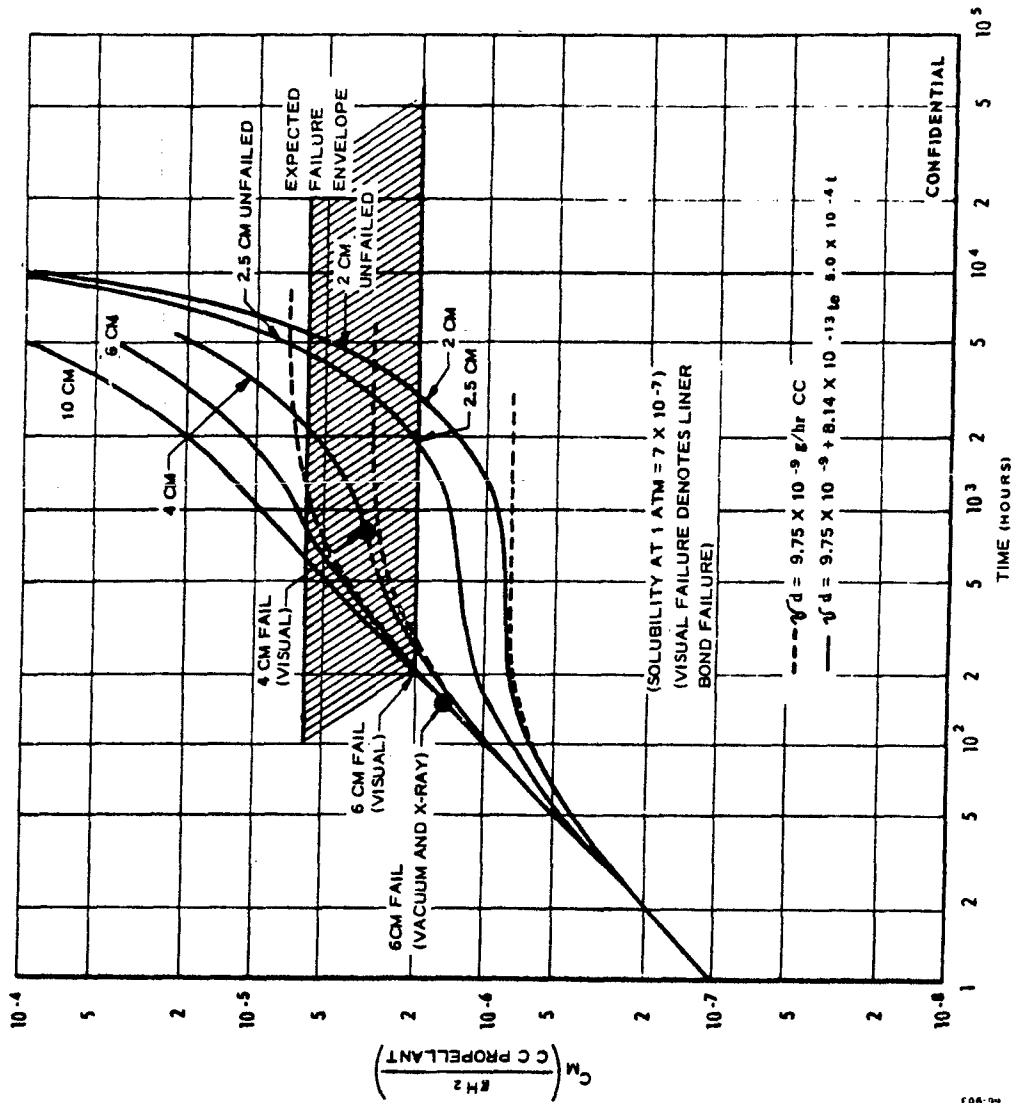


Figure 12 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 75°F with Undoped LMH-1 (Blend 97-131)

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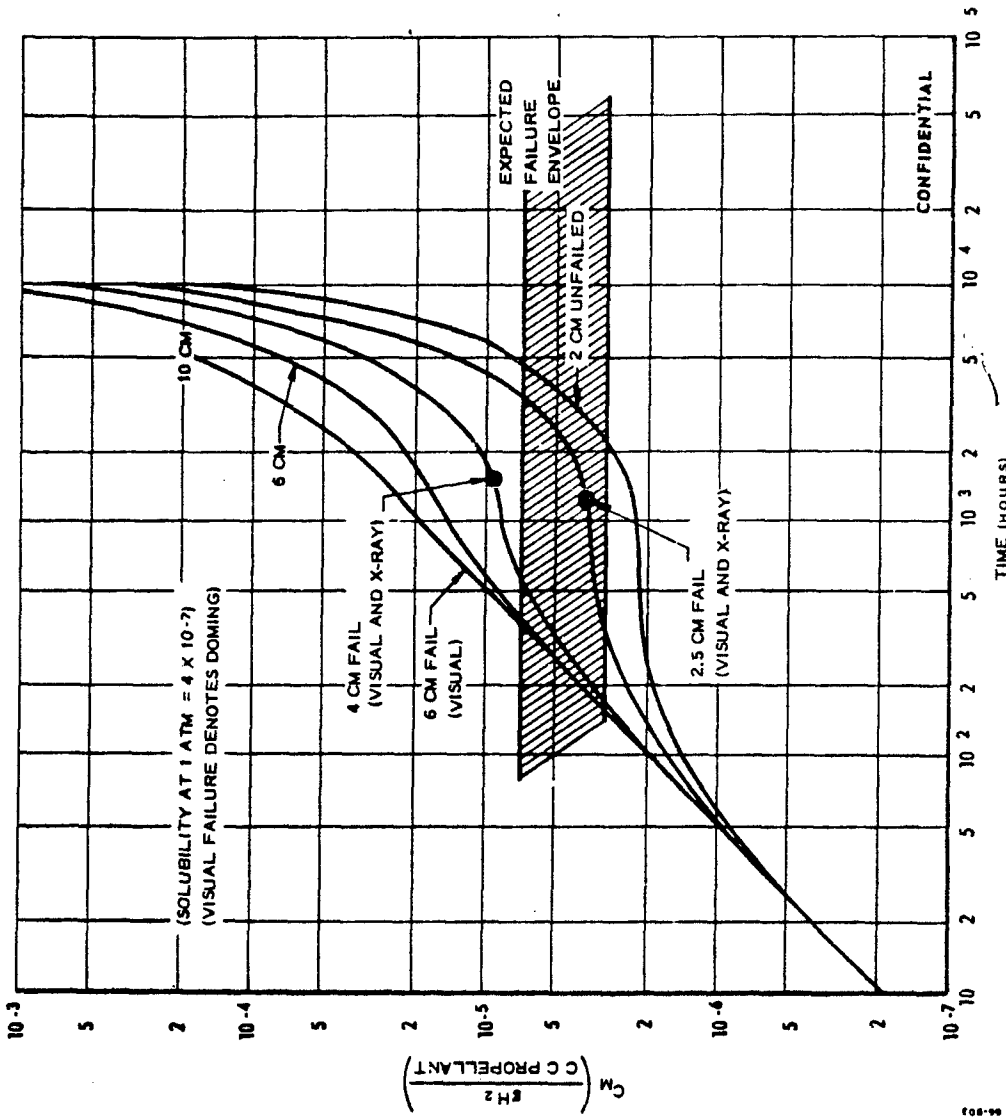


Figure 13 Calculated Maximum Gas Concentration in ABL-FHA at 75°F with Undoped LMH-1 (Blend 97-131)

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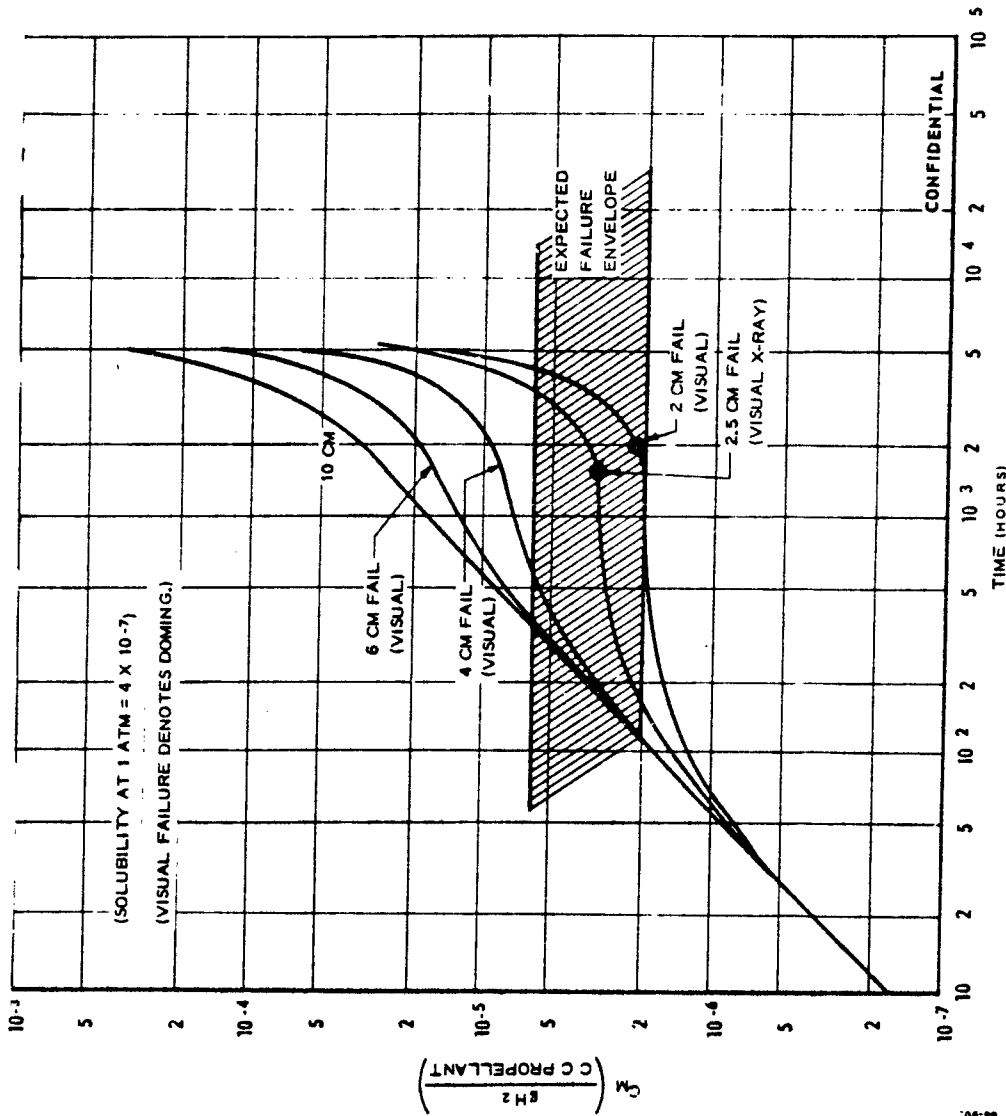


Figure 14 Calculated Maximum Gas Concentration in UTP-6814 Propellant at 75° F with Undoped LMH-1 (Blend 97-131)

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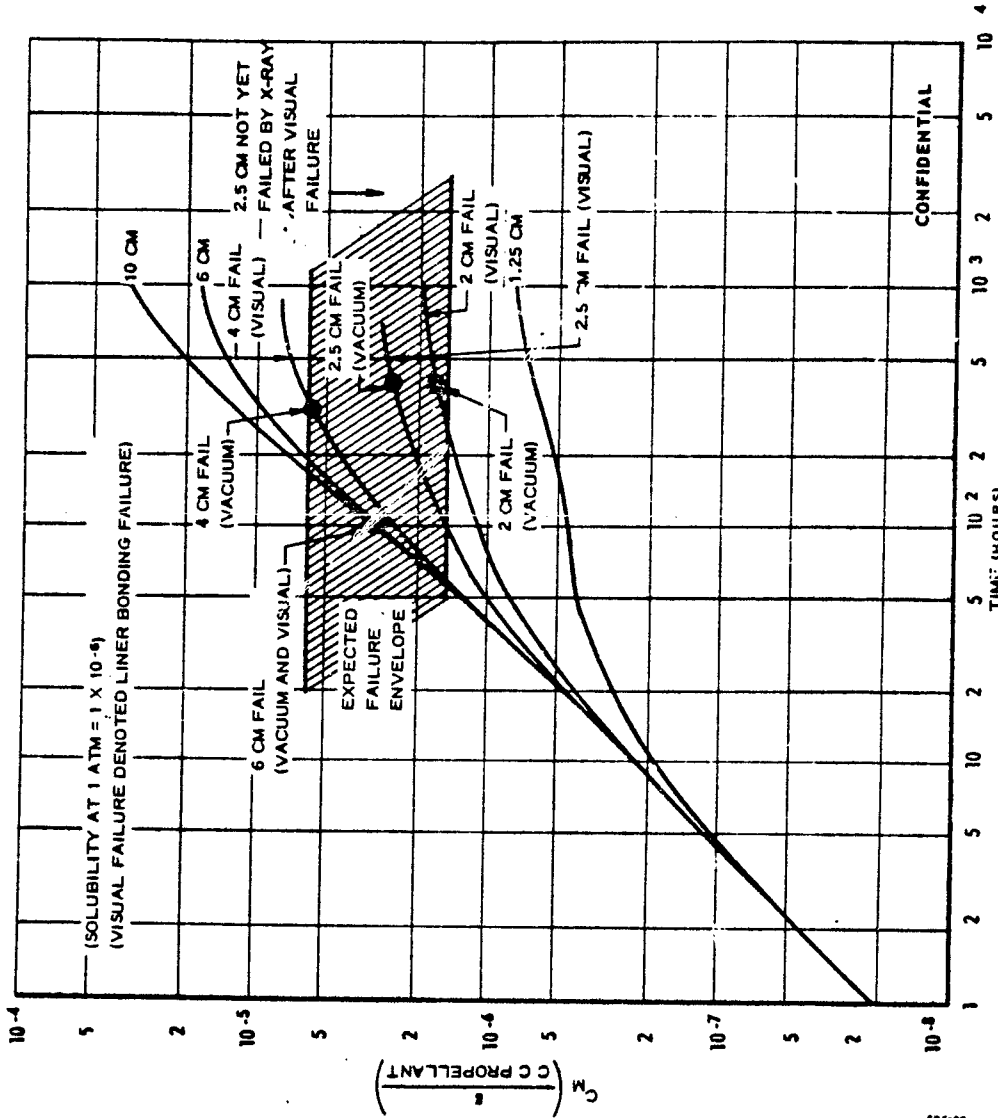


Figure 15 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 115°F with Mg-doped LMH-1 (Lot 03296)

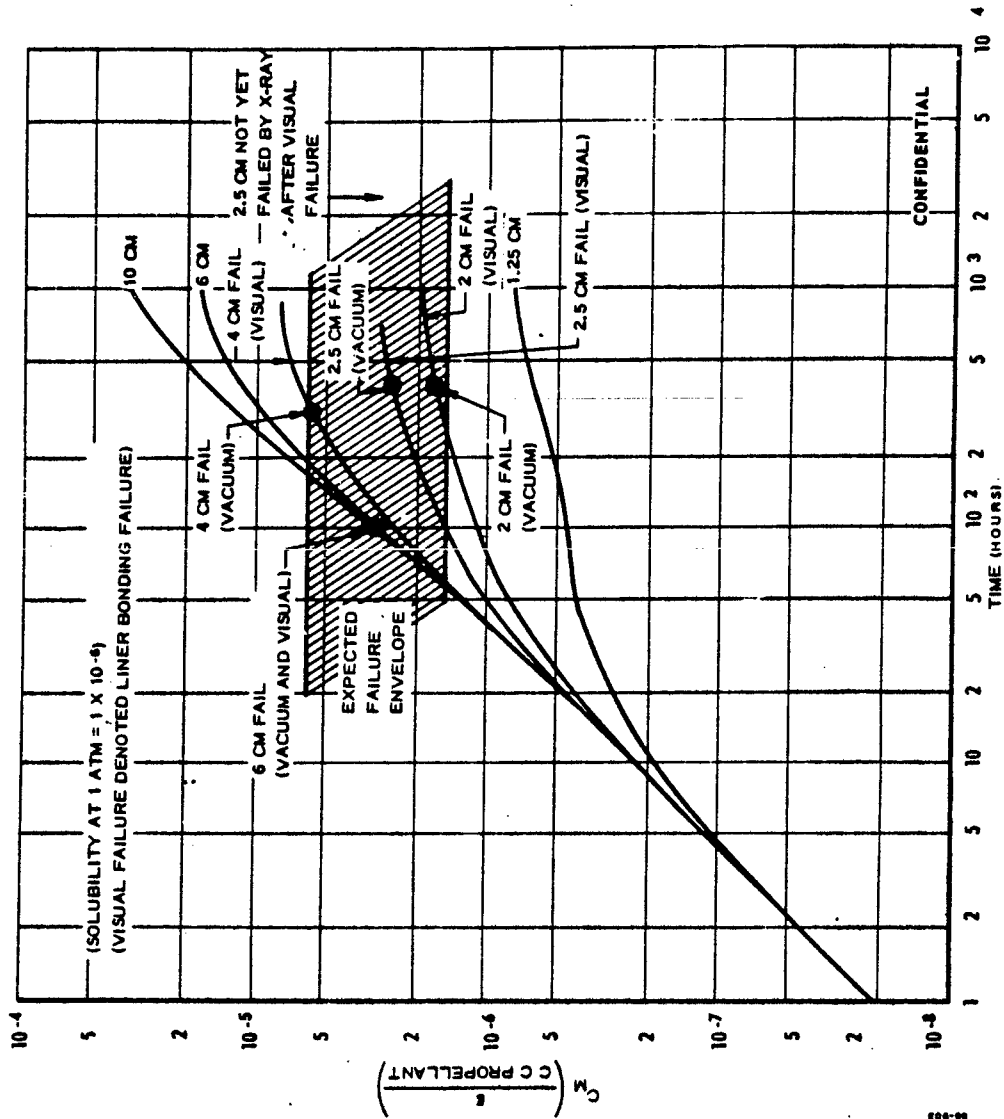


Figure 15 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 115°F with Mg-doped LMH-1 (Lot 03296)

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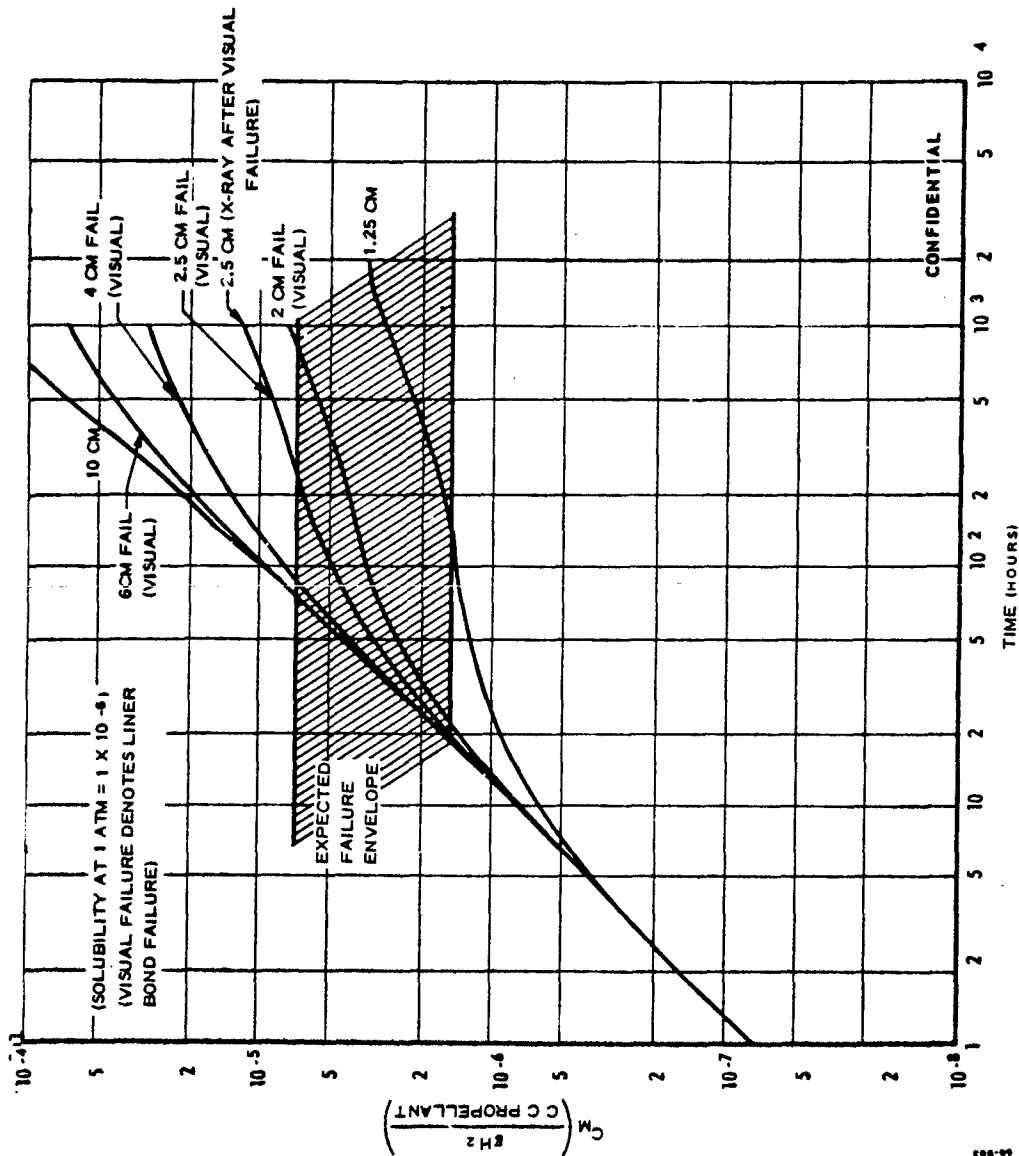


Figure 16 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 115°F with Mg-doped LMH-1 (Lot 07146)

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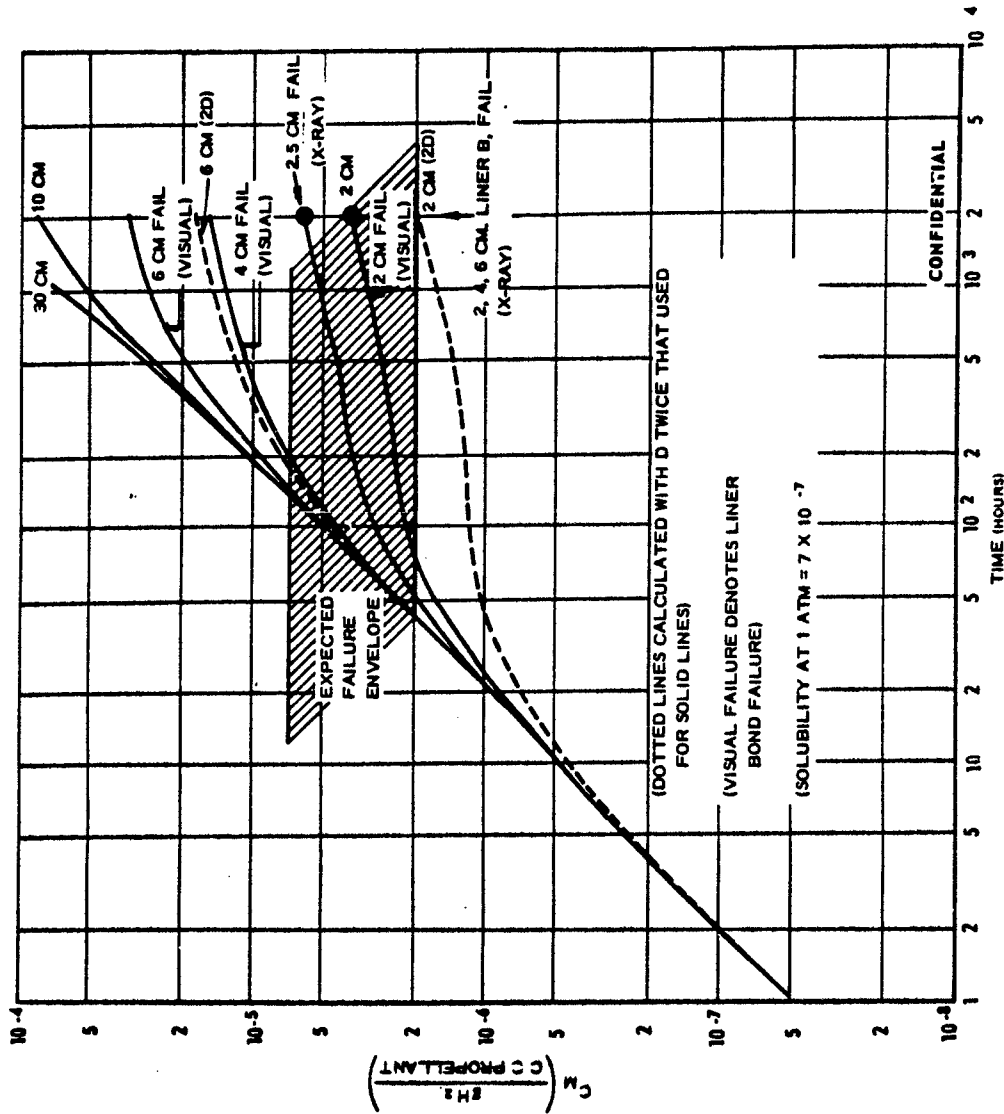


Figure 17 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 100°F with Doped LMH-1 (Lot 07146)

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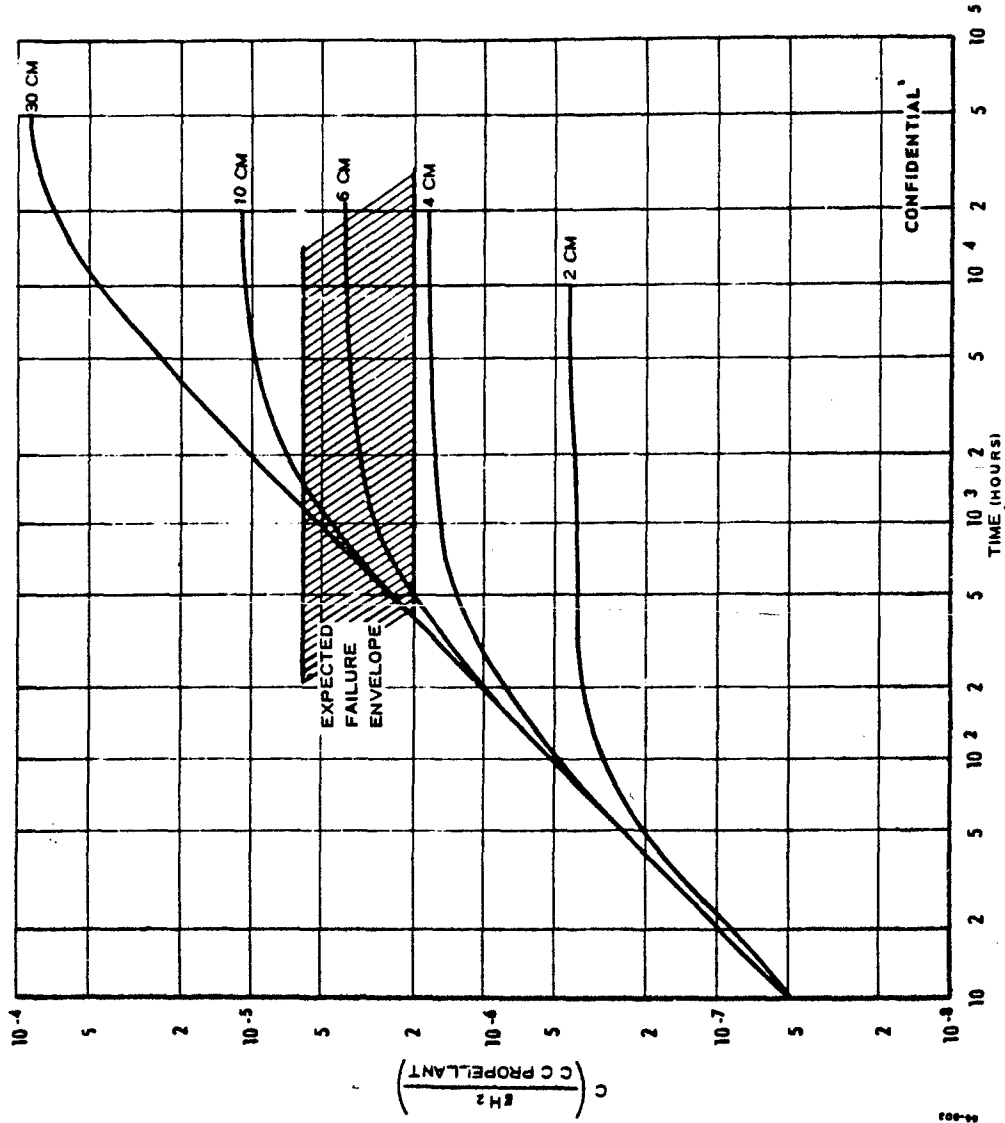


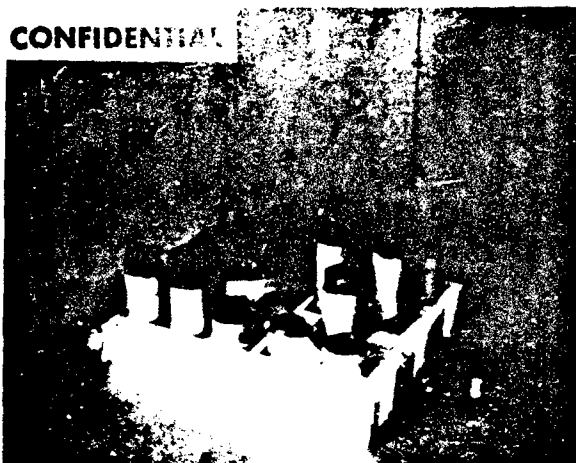
Figure 18 Calculated Maximum Gas Concentration in LPC-A23-06 Propellant at 75°F with Mg-doped LMH-1 (Lot 03296)

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LPC A23-06 20 DAYS AFTER  
FIRST APPEARANCE OF FAILURE.  
SAMPLE AT UPPER RIGHT IS A CONTROL.



UTP-6814. 4 DAYS AFTER  
FIRST DOMING. SAMPLES  
AT LEFT ARE CONTROLS

Figure 19 Surveillance Samples After Failure (115°F)

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(C) c. Discussion of Results

(U) In the following, the impact of uncertainties in the theoretical analysis, and of uncertainties (errors) in the experimental determination of critical parameters upon shelflife prediction will be reviewed.

(1) Limiting Gas Concentration

(U) A key item in this shelflife analysis involves the estimate of limiting gas concentrations, which in turn are related to failure mechanism. If failure mechanism, and thereby limiting gas concentrations, could be stated with accuracy, the need for an experimental surveillance program would be largely voided. A primary purpose of the surveillance program was thus to verify that failure will occur within the expected range of internal gas pressure. In other words, the surveillance program served as an experimental means of determining propellant internal stress capability.

Possible sources of error, and the effects upon shelflife prediction, are as follows:

- (C) ● The predicted concentration-to-failure for the 75<sup>0</sup>F test samples is based upon extrapolated values for the AlH<sub>3</sub> rate of decomposition. The latter data need experimental verification using a more sensitive experimental method (e. g. , mass spectrometer) than was used in this study. In this context it is noted that few, if any, of the published data on AlH<sub>3</sub> decomposition rates sufficiently emphasize the rates of gas generation within the induction period (~ first 0.1 percent decomposition) which is the period of importance for AlH<sub>3</sub> propellant shelflife.
- (U) ● The situation with the low temperature (75<sup>0</sup>F) shelflife predictions based upon high temperature surveillance might be aggravated further by differences in failure mechanism. It is conceivable that a very gradual increase in internal gas pressure (low temperature) will produce microporosity via a liquid displacement (creep) mechanism, while a more rapid pressure buildup (high temperature) will produce rupture (cracks). Assuming a greater rupture stress (product of E and  $\phi$ , equation 2) and lower rupture elongation at higher strain rates, the failure pressure observed at high temperatures may be greater than that at low temperatures. Thus, a predicted shelflife at low temperature based upon high temperature observations could be erroneously high.
- (U) ● No gas solubility and diffusion rate measurements were performed with porous control propellants, largely because of experimental difficulties in introducing the

desired degree of porosity into the samples. However, the presence of porosity (cracks or bubbles) can be expected to increase the effective diffusion rate and solubility. Thus, the calculated failure pressures (Table XVI) could be at disparity with the effective failure pressures by a significant margin if the test sample exhibited initial porosity. This effect would result in erroneously long predicted shelflives for large web thickness. (This conclusion may be substantiated by examination of the effect of increased diffusion coefficient shown in Figure 17.)

- (U)
  - Initial failure with numerous surveillance test samples occurred within the case/liner/propellant interface. If this failure occurred along the container walls, the effective sample length (diffusional path) was significantly shortened. This will result in a lower than expected gas pressure, and better than predicted shelf-life, and the effects would be more pronounced with the 1.1-inch ID samples than the 2.5-inch ID samples. As a result, the data obtained with the latter samples (2.5-inch ID) are weighed more heavily. Failure within the interfacial region (side walls) would again result in erroneously long predicted shelflife for large web thicknesses---in a similar manner as with the effects of porosity.
- (U)
  - Built-in stresses (e. g. , cure shrinkage stress) would lower the effective stress capability of the propellant, and would thereby lower the maximum permissible gas concentration. This effect, which penalizes shelflife, would be more pronounced with the 6-cm (1.1-inch ID) samples than with the 2, 2.5, or 4-cm samples. Calculations of the cure and thermal shrinkage stresses in these specimens show these effects to be negligible only in the 2-cm (1.1-inch ID) and the 2.5-cm (4-inch ID) specimens.

(C) (2) Propellant Mechanical Properties

The a priori estimate of limiting internal gas concentration is based upon propellant mechanical property data. Table XVI presents some physical property data for the UTC, ABL, and LPC surveillance propellants. Detailed data are available only for the UTP-6814 (Ref. 10), particularly as concerns data at the very low strain rates applicable to the failure processes for unstabilized LMH-1 at 75°F and stabilized LMH-1 at 115°F or below. The properties for the LPC and ABL (Ref. 11) propellants are estimated from the behavior of similar non-LMH-1 formulations. Assuming the validity of equation (2), the calculated pressures to rupture a spherical bubble indicate that the dissolved gas concentrations at such rupture will be from 3 (LPC at 115°F) to 7 (UTC at 75°F) times greater than the

TABLE XVI  
MECHANICAL PROPERTIES OF PROPELLANT SURVEILLANCE SYSTEMS

System	Max. Stress (psi at 0.74 min. strain rate)	Strain at Max. Stress (% at 0.74 min. strain rate)	Secant Modulus (psi at 0.74 min. strain rate)	Strain at Rupture (% at 0.074 min. strain rate)	Modulus (psi at $6 \times 10^{-4}$ min. strain rate)	Rupture Pressure (psi)	Rupture Concentration (d) (g H <sub>2</sub> /cc propellant)
UTP-6814 115°F 75°F	63 80	16 15	400 530	16 16	230 400	<sup>(b)</sup> 56 <sup>(b)</sup> 97 (4 atm) (7 atm)	$2.8 \times 10^{-6}$
LPC-A23-06(a) 115°F 75°F	~60 ~110	~40 ~50	150 220		~100 ~150	~45 <sup>(c)</sup> ~75 <sup>(c)</sup> (3 atm) (5 atm)	$3.0 \times 10^{-6}$ $3.5 \times 10^{-6}$
5ABL-FHA(a) 75°F	100	35	300		~200	~82 <sup>(c)</sup> (6 atm)	$2.8 \times 10^{-6}$

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- (a) Estimated from similar non LMH-1 formulations.  
 (b) Calculated from equation (2), using E at  $6 \times 10^{-4}$  min.<sup>-1</sup> strain rate and  $\phi$  at 0.074 min.<sup>-1</sup>.  
 (c) Calculated from equation (2), using E at  $6 \times 10^{-4}$  min.<sup>-1</sup> strain rate and  $\phi$  at 0.74 min.<sup>-1</sup>.  
 (d) Rupture pressure in atm. times measured solubility at one atm.

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measured solubilities at one atmosphere. The pressures required to initiate the bubble formation will be less than the rupture values; for example the product E  $\phi$  using the low strain-rate values for UTP-6814 is 64 psi at 75°F and 37 psi at 115°F. While all these values must be accepted with some reservation at present, they do provide additional guidelines in gauging the reasonableness of the comparisons in Figures 12 through 18. If we place primary emphasis upon the 2 and 2.5-cm samples and failure detection by vacuum swelling and X-ray, it may be seen that the calculated rupture concentrations in Table XVI are in agreement with observed values within a factor of 2 to 3.

(C) d. Implications (Prediction of Large Motor Shelflife)

(C) With the above comments and guidelines in mind, shelflife predictions for web thicknesses greater than 4 inches have been made and are presented in Table XVII. Due to the errors noted above, these estimates cannot be very precise at this time, but they certainly suffice to demonstrate that the most stable LMH-1 sample employed in this study (Mg-doped Lot 03296) hardly produces a long-term storable propellant.<sup>7</sup>

(U) Several more detailed comments regarding these predictions are in order:

- (U) • While the predictions are based upon a rectangular geometry and linear diffusion (in effect a slab whose thickness,  $l$ , is small relative to its other dimensions), within the errors involved the predictions should also apply to a cylindrical, case bonded, interior bore motor of the same web thickness,  $l$ . Obviously, they apply directly to case bonded end burning motors of length,  $l$ . A star-centered grain will, of course, possess an  $l$  value somewhat greater than the distance from case to star valley.
- (C) • In the linear portion of the calculated concentration-time curves (Figures 12 through 18) the concentration is relatively independent of web thickness as long as the latter exceeds about 4 inches. Thus, failure concentrations and shelflives falling in that region will also be independent of web thickness above 4 inches. If the gas generation rate should fall sufficiently--or the diffusion constant rise--the concentration curves could drop such that the failure concentrations fall within the asymptotic (steady state) region for greater  $l$  values than is presently the case. For example, in Figure 18 the 2, 4 and possibly 6-cm specimens may well never fail in the absence of pronounced increases in gas generation rate or deterioration in physical

<sup>7</sup>Again, it should be noted that the  $AlH_3$  samples employed in this study do not represent the most stable materials now available.

TABLE XVII  
PREDICTED SHELF LIFE OF LMH-1 PROPELLANT  
CONTAINING LMH-1 SAMPLES EMPLOYED IN THIS STUDY

<u>System</u>	<u>Shelflife for Web Thickness Above 4-in.</u>
A. Undoped LMH-1	
(1) LPC-A23-06, 75°F	200 - 600 hours
(2) ABL-FHA, 75°F	150 - 350 hours
(3) UTP-6814, 75°F	120 - 350 hours
B. Mg-doped (Lot 07146)	
(4) LPC-A23-06, 100°F	40 - 130 hours
(5) LPC-A23-06, 115°F	20 - 65 hours
C. Mg-doped (Lot 03296)	
(6) LPC-A23-06, 115°F	50 - 170 hours
(7) LPC-A23-06, 75°F	400 - 1500 hours (a)

Note: (a) Errors in extrapolating the gas generation rate could perhaps be expected to double the breadth of this range.

properties.<sup>8</sup> On the other hand a three to four-fold increase in LMH-1 stability above that of the particular sample used would be necessary before a 10-cm system could last for more than about one year, and at least a 10-fold increase in LMH-1 stability would be required for one-year shelflife of a 30-cm web thickness motor.

- (C) • The apparently greater shelflife of the LPC propellant over that of the ABL or UTC propellants is not a demonstration that the first employs a more suitable binder for LMH-1. Instead, it is a reflection primarily of the low solids content of the experimental, non-optimized LPC propellant which results in effectively greater diffusion constant and solubility. In actual fact, there is at least some evidence from the X-rays that the LPC double-base binder is the least effective of the three in that it is more prone to rupture ("macroscopic" failure → fine cracks) whereas the other two crosslinked binders--and particularly the UTC--tend to go through a more extended microporous stage prior to rupturing.

(U) e. Critique of Experimental Technique Used

In hindsight, the surveillance specimens employed in this study, placing large emphasis upon the case/liner/propellant bond and emphasizing internal stress conditions, possessed definite drawbacks and limited the accuracy in defining experimental time-to-failure; the use of larger and unbonded test specimens is indicated for seeking a more precise index of correlation between prediction and test. In addition, the failure process (mechanism) requires further analysis with reference to: the effects of rates of pressure (stress) application; the effects of the transition between initial microscopic failure (microporosity) and rupture; the effects of binder structure upon this transition; and the effects of binder-solids adhesion. Pertinent studies will serve not only for improving our ability to predict shelflife, they are expected to lead to potential improvements in shelflife itself.

(C) 7. CONCLUSIONS

(C) The program conducted under this contract has resulted in the ability to predict large-motor shelflife ( $\text{AlH}_3$  propellants) within reasonable accuracy (factor of 2 to 3). As such, the program has served to define thermal stability goals for the  $\text{AlH}_3$  material development programs. Moreover, since general agreement between the experimental and the calculated shelflife data was obtained, the existing analyses (models) can serve as a starting point for the precise prediction of usable motor shelflife under more complex motor histories (e. g., temperature cycling; aging).

<sup>8</sup>In practice this means that surveillance specimens containing this LMH-1 sample at 75°F would have to possess diffusion path lengths of at least 6-cm.



(C) As would be expected, various shortcomings were found to be associated with the approaches taken; these shortcomings will need to be corrected in refining the analyses and predictions. The key areas for such improvements or refinements are as follows:

- (C) ● There is need for better methods for measuring  $\text{AlH}_3$  thermal stability. Propellant failure occurs well before 0.1 percent of the hydride has decomposed, i. e. , within the induction period for the hydride decomposition. This calls for more emphasis on studies dealing with the phenomena which affect the induction period and for more emphasis upon that period in rating materials as to relative stability.
  - (U) ● There is need to arrive at a better understanding of failure mechanism to permit a more precise definition of limiting gas concentrations; alternatively, the development of direct methods for measuring critical interior gas pressure would be most desirable.
  - (U) ● There is need to develop better experimental techniques for defining time-to-failure, taking into account differences in the failure mechanism. This includes the use of surveillance test samples which permit a more independent analysis of propellant and propellant/liner failures. Implicit here is the need for a more precise definition of those propellant grain conditions which truly constitute practical failure, e. g. , microporosity or cracks.
- (U) Related studies are not only expected to improve the ability to predict shelflife, but can be expected to result in significant improvements in shelflife itself.

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**SECTION IV**

**FUTURE WORK**

- (C) Product evaluation services will be provided Ethyl Corporation on production samples of LMH-2. The two major criteria are propellant processibility (mix viscosity) and the effectiveness of passivation treatments. Emphasis will be shifted from Beany to the continuous process materials and the fluid pressure crystallized forms as these become available.
- (C) Simulated scale-up procedures for passivation of ground Beany will be evaluated.
- (C) Surface area measurements and correlations with burning rate and combustion efficiency will be continued.
- (C) Tracer studies on the passivation chemistry of LMH-2 will be initiated.
- (C) Differential scanning calorimetry studies of the decomposition kinetics of LMH-2 will begin.

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SECTION V

BERYLLIUM HEALTH PHYSICS PROGRAM

(U) A summary of all monitoring sample data taken from 12 December through 15 February is given in Table XVIII.

(U) During this period, air monitors in Building 119A laboratory were run during all working hours, the filters being analyzed for Be every 15 working days or more frequently, depending upon the work load in the laboratory.

TABLE XVIII  
BERYLLIUM MONITORING DATA

Laboratory, Building 119A(a)	Dec 12-Dec 27 (10 days)	Dec 28-Jan 10 (8 days)	Jan 11-Jan 31 (15 days)	Feb 1-Feb 15 (11 days)
Sample Station No. 1				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	1.4	NIL (b)	0.6	1.0
μg Be/m <sup>3</sup>	0.02	-	NIL	0.015
Sample Station No. 2				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	0.2	NIL	NIL	1.0
μg Be/m <sup>3</sup>	NIL	-	-	0.015
Sample Station No. 3				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	NIL	NIL	NIL	1.0
μg Be/m <sup>3</sup>	-	-	-	0.015
Sample Station No. 4				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	0.2	NIL	NIL	0.4
μg Be/m <sup>3</sup>	NIL	-	-	NIL
Sample Station No. 5				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	NIL	NIL	NIL	0.4
μg Be/m <sup>3</sup>	-	-	-	NIL
Sample Station No. 6				
m <sup>3</sup> air sampled	60	48	90	66
μg Be	NIL	NIL	NIL	1.3
μg Be/m <sup>3</sup>	-	-	-	0.02

(b) &lt; 0.1 μg Be

(a) Location of Laboratory Building 119A Samplers

Sample Station No. 1A	Outside air lock, small dry box
Sample Station No. 2	Front of small dry box
Sample Station No. 3	Over sink
Sample Station No. 4	Front of hood
Sample Station No. 5	Front of large dry box
Sample Station No. 6	Outside air lock, large dual dry box

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14. KEY WORDS	LINK A		LINK B		LINK C	
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